**Atmospheric
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New and extended parameterization of the thermodynamic model AIOMFAC: calculation of activity coefficients for organic-inorganic mixtures containing carboxyl, hydroxyl, carbonyl, ether, ester, alkenyl, alkyl, and aromatic functional groups

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Abstract

We present a new and considerably extended parameterization of the thermodynamic activity coefficient model AIOMFAC (Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients) at room temperature. AIOMFAC combines a Pitzer-like electrolyte solution model with a UNIFAC-based group-contribution approach and explicitly accounts for interactions between organic functional groups and inorganic ions. Such interactions constitute the salt-effect, may cause liquid-liquid phase separation, and affect the gas-particle partitioning of aerosols. The previous AIOMFAC version was parameterized for alkyl and hydroxyl functional groups of alcohols and polyols. With the goal to describe a wide variety of organic compounds found in atmospheric aerosols, we extend here the parameterization of AIOMFAC to include the functional groups carboxyl, hydroxyl, ketone, aldehyde, ether, ester, alkenyl, alkyl, aromatic carbon-alcohol, and aromatic hydrocarbon. Thermodynamic equilibrium data of organic-inorganic systems from the literature are critically assessed and complemented with new measurements to establish a comprehensive database. The database is used to determine simultaneously the AIOMFAC parameters describing interactions of organic functional groups with the ions H^+, Li^+, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Cl^-, Br^-, NO_3^-, HSO_4^-, and SO_4^{2-}. Detailed descriptions of different types of thermodynamic data, such as vapor-liquid, solid-liquid, and liquid-liquid equilibria, and their use for the model parameterization are provided. Issues regarding deficiencies of the database, types and uncertainties of experimental data, and limitations of the model, are discussed. The challenging parameter optimization problem is solved with a novel combination of powerful global minimization algorithms. A number of exemplary calculations for systems containing atmospherically relevant aerosol components are shown. Amongst others, we discuss aqueous mixtures of ammonium sulfate with dicarboxylic acids and with levoglucosan. Overall, the new parameterization of AIOMFAC agrees well with a large number of experimental datasets. However, due to various reasons, for certain mixtures important deviations can occur. The new parameterization makes AIOMFAC a

versatile thermodynamic tool. It enables the calculation of activity coefficients of thousands of different organic compounds in organic-inorganic mixtures of numerous components. Models based on AIOMFAC can be used to compute deliquescence relative humidities, liquid-liquid phase separations, and gas-particle partitioning of multicomponent mixtures of relevance for atmospheric chemistry or in other scientific fields.

1 Introduction

Thermodynamic models are key tools to gain insight into the non-ideal behavior of organic-inorganic mixtures. Atmospheric aerosols present prominent examples for organic-inorganic mixtures of remarkable complexity, containing a multitude of different organic compounds, inorganic salts and acids, and water (e.g., Rogge et al., 1993; Saxena and Hildemann, 1996; Murphy and Thomson, 1997; Middlebrook et al., 1998; Decesari et al., 2000; Lee et al., 2002; Griffin et al., 2002; Maria et al., 2004; Kanakidou et al., 2005; Murphy et al., 2006; Decesari et al., 2006; Zhang et al., 2007; Russell et al., 2009). Gas-particle partitioning of water and semivolatile organic and inorganic compounds is determined by thermodynamic equilibrium between the gaseous and condensed phases (Pankow, 1994, 2003; Hallquist et al., 2009; Zuend et al., 2010) and by the kinetics of exchange processes such as gas phase diffusion (Marcolli et al., 2004b). The non-ideality of mixtures in aerosol particles influences the gas-particle partitioning and affects the physical state of the condensed phase, potentially leading to liquid-liquid phase separation (Pankow, 2003; Erdakos and Pankow, 2004; Marcolli and Krieger, 2006; Chang and Pankow, 2006; Ciobanu et al., 2009; Zuend et al., 2010; Kwamena et al., 2010; Smith et al., 2011), the formation of crystalline solid phases (Nenes et al., 1998; Clegg et al., 1998a; Colberg et al., 2004; Zaveri et al., 2005; Fountoukis and Nenes, 2007), or the transition to an amorphous solid state (Zobrist et al., 2008, 2011; Murray, 2008; Mikhailov et al., 2009; Virtanen et al., 2010).

Inorganic salts and acids (electrolytes) that for the most part dissociate into ions (charged molecules or atoms) in liquid solutions play an important role in aqueous

organic-inorganic systems. Interactions between ions and neutral organic molecules may have a crucial impact on the dissolution behavior and phase state of a system, commonly known as the salt-effect: Increasing the concentration of a strong electrolyte in a mixture may lead to "salting-out" of relatively nonpolar organics, i.e., the dissolved ions drive the organic compounds out of the mixed phase – either to the gas phase or into a different, organic-rich liquid phase, initiating or modifying a liquid-liquid phase separation and a new equilibrium state. This well-known property of electrolytes is used in chemical and biochemical process engineering to separate aqueous organic mixtures (liquid-liquid extraction, two-phase partitioning) and to shift azeotropes in distillation processes, with large-scale applications in the petrochemical industry, in seawater desalination plants, and water purification systems. With respect to tropospheric aerosols, recent modeling studies (Zuend et al., 2010) and experiments (Smith et al., 2011) on the phase state of idealized laboratory organic-inorganic aerosol mixtures suggest that ambient aerosols likely exhibit liquid-liquid phase separation at relative humidities (RH) ≲ 85%.

Activity coefficients of the different components represent the degree of thermodynamic non-ideality in a specific multicomponent mixture, caused by the combined effects of all molecular interactions. For atmospheric purposes the vapor pressures of water and semivolatile organic and inorganic compounds are required in gas-particle partitioning calculations, which depend on the saturation vapor pressures of the pure compounds and their activity coefficients in the liquid aerosol mixture. For example, in case of water, the equilibrium water vapor pressure over a liquid mixture, p_w, is related to the water activity on the mole fraction basis (denoted by superscript (x)), $a_w^{(x)}$, by $p_w = p_w^\circ a_w^{(x)}$, where p_w° is the saturation vapor pressure over pure liquid water (a function of temperature only). Activity and activity coefficient, $\gamma_s^{(x)}$, of a compound s are related by $a_s^{(x)} = \gamma_s^{(x)} x_s$, where x_s is the mole fraction of s in the liquid mixture. These basic thermodynamic relationships, corresponding chemical potentials and standard states, are described in detail by Zuend et al. (2010). In case of atmospheric water at gas-particle equilibrium, relative humidity and aerosol water activity are related by

$RH = a_w^{(x)} = \gamma_w^{(x)} x_w$ (strictly valid only for droplet sizes where the Kelvin effect due to the curvature of the surface can be neglected, i.e., for droplet diameters > 100 nm). At the core of thermodynamic equilibrium calculations are therefore models to calculate activity coefficients.

In the past, the development of activity coefficient models mainly evolved in two categories: (1) models for (organic-free) aqueous electrolyte solutions or for (electrolyte-free) aqueous organic mixtures, and (2) models for mixed organic-inorganic systems. In category (1), a number of successful models for calculating thermodynamic aerosol properties of aqueous electrolyte mixtures have been developed based on Pitzer's extension of the Debye-Hückel theory and the Pitzer-Simonson-Clegg approach (e.g., Clegg and Pitzer, 1992; Clegg et al., 1992; Carslaw et al., 1995; Clegg et al., 1998a,b; Topping et al., 2005a; Amundson et al., 2006; Zuend et al., 2008) or the Kusik-Meissner relationship and Bromley's formula (Nenes et al., 1998; Fountoukis and Nenes, 2007). Aerosol models for mixtures of organics and water are most often based on the UNIQUAC model (Abrams and Prausnitz, 1975) or its group-contribution version UNIFAC (Fredenslund et al., 1975; Hansen et al., 1991). Models for organic-inorganic mixtures are generally composed of an aqueous electrolyte term, an (aqueous) organic term, and an organic-ion mixing term (Tong et al., 2008). In category (2), models for organic-inorganic mixtures can be further categorized into (i) so-called decoupled models, where an explicit organic-ion mixing term is not considered, and (ii) fully coupled models, as described in detail by Tong et al. (2008). Decoupled organic-inorganic models are based on combinations of existing approaches for the electrolyte part and the organic part, and a mixing rule such as the Zdanovskii-Stokes-Robinson (ZSR) scheme (Zdanovskii, 1936, 1948; Clegg et al., 2003; Clegg and Seinfeld, 2004) is used to calculate the water content of mixtures. Examples of such decoupled models are the approach by Clegg et al. (2001) and the aerosol diameter dependent equilibrium model (ADDEM) of Topping et al. (2005b). Hybrid approaches to combine two specific models, of which one describes the inorganic part and the other the organic part, have been discussed by Clegg and Seinfeld (2006a). Many coupled organic-inorganic models for

aerosols are based on an extended UNIFAC approach (e.g. Ming and Russell, 2002; Raatikainen and Laaksonen, 2005; Chang and Pankow, 2006; Erdakos et al., 2006; Zuend et al., 2008), differing mainly in the degree of detail regarding the description of aqueous electrolyte solutions and the coupling via an organic-inorganic interaction part, as discussed by Zuend et al. (2008).

Tong et al. (2008) compared four different organic-inorganic models, two of which are fully coupled, to test whether the inclusion of explicit ion-organic interaction terms improves the performance over that of decoupled models. They tested this question by comparison of model predictions with experimental water activity data of dicarboxylic acids mixed with NaCl or $(NH_4)_2SO_4$. Tong et al. found for the systems studied, that the decoupled models performed as well as the coupled models and in some cases even better. However, water activity predictions show only the abilities of thermodynamic models to calculate particle water content, but not the ability to correctly calculate the activity coefficients of all components. In fact, for systems of more than two components, a thermodynamic model might accurately predict water activities, while failing to accurately predict activities of the other components. As we point out in this study, a rigorous thermodynamic calculation of the activity coefficients of all species in a system is essential to accurately compute vapor-liquid, liquid-liquid, and solid-liquid equilibria, and, hence, the gas-particle partitioning and phase states. The AIOMFAC model, described in the following sections, is a fully coupled model that allows consistent calculations of activity coefficients and phase states. This is essential for a proper description of mixed tropospheric aerosols, which are expected to exhibit liquid-liquid phase separation at RH $\lesssim 85\%$ (Zuend et al., 2010; Smith et al., 2011).

2 AIOMFAC model

The thermodynamic model AIOMFAC (Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients) is a group-contribution model designed for the calculation of activity coefficients in aqueous organic-inorganic systems (Zuend et al., 2008).

The group-contribution concept treats organic molecules as structures composed of different functional groups. This approach allows the representation of thousands of different organic compounds using a relatively small and manageable number of functional groups. Especially regarding the organic aerosol fraction, a compound-specific approach may not be feasible except in the case of well-defined laboratory systems. Field studies reporting important individual organic compounds, compound classes, and/or distributions of functional groups found in ambient aerosols, identified alkyl, carboxyl, hydroxyl, ketone, aldehyde, amines, organosulfates, ether, alkenyl, and aromatic groups (Decesari et al., 2000; Maria et al., 2003; Decesari et al., 2006; Russell et al., 2009; Gilardoni et al., 2009; Liu et al., 2009; Takahama et al., 2011). Hence, many organic aerosol components can be characterized by means of about 10 different kinds of organic functional groups.

AIOMFAC is based on the group-contribution model LIFAC (Yan et al., 1999) – yet modified in many respects to better represent relevant species, reference states, and the relative humidity range of the atmosphere. This is described in our previous work (Zuend et al., 2008), where we we have considered cations H^+, Li^+, Na^+, K^+, NH_4^+, Mg^{2+}, and Ca^{2+}, anions Cl^-, Br^-, NO_3^-, HSO_4^-, and SO_4^{2-} and a wide range of alcohols/polyols composed of the alkyl (CH_n, n = 0, 1, 2, 3) and hydroxyl (OH) functional groups for a first parameterization of organic-inorganic interactions.

In this study, we revise and extend the AIOMFAC model parameterization for the full range of atmospheric compositions covering activity coefficient calculations of mixtures containing carboxyl, hydroxyl, ketone, aldehyde, ether, ester, alkenyl, alkyl, aromatic carbon, and aromatic carbon-alcohol functional groups, plus water and the inorganic ions as given above. We discuss how the availability, reliability, and abundance or in some cases lack of experimental data, define the main limitations for the current parameterization of the different binary functional group $\leftrightarrow$ ion interactions (the double arrow $\leftrightarrow$ is used to mark interactions). The semi-empirical middle-range parameterization of explicit organic $\leftrightarrow$ inorganic interactions in organic + water + salt solutions enables accurate and thermodynamically consistent computations of activity coefficients for all

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mixture species, required for the prediction of vapor-liquid equilibria (VLE), solid-liquid equilibria (SLE), liquid-liquid equilibria (LLE), and the computation of gas/particle partitioning of multicomponent systems (Zuend et al., 2010). It should be noted that, similar to the previous version, the model so far is constrained to room temperature. Generalizations of the model applicable to other temperatures are presently underway.

3 Methods

3.1 Activity coefficients in AIOMFAC

Molecular interactions in liquid mixtures containing ions and neutral species are represented by AIOMFAC using thermodynamic expressions for long-range (LR), middle-range (MR), and short-range (SR) contributions (Zuend et al., 2008). These three interaction ranges contribute to the Gibbs excess energy $G^{\mathrm{ex}}(p,T,n_j)$ of a thermodynamic system, constituting the system's deviation from an ideal mixture:

$$G^{\mathrm{ex}}(p,T,n_j) = G^{\mathrm{ex}}_{\mathrm{LR}} + G^{\mathrm{ex}}_{\mathrm{MR}} + G^{\mathrm{ex}}_{\mathrm{SR}}. \tag{1}$$

Here, p is the total pressure, T the absolute temperature, and n_j ($j = 1,\ldots,k$) the molar amounts of the k components in a system. Mole fraction based activity coefficients $\gamma_j^{(x)}$ of the different components are derived from expressions for the different parts of G^{ex} using the relation

$$\ln\gamma_j^{(x)} = \left[\frac{\partial G^{\mathrm{ex}}/(RT)}{\partial n_j}\right]_{p,T,n_{j'\neq j}}, \tag{2}$$

where R is the universal gas constant. Accordingly, the activity coefficients are calculated from the three model parts:

$$\ln\gamma_j^{(x)} = \ln\gamma_j^{(x),\mathrm{LR}} + \ln\gamma_j^{(x),\mathrm{MR}} + \ln\gamma_j^{(x),\mathrm{SR}}. \tag{3}$$

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The long-range part, an extended Debye-Hückel expression, and the semi-empirical middle-range part form together a Pitzer-like group-contribution model, enabling accurate descriptions of electrolyte solutions, from dilute to highly concentrated conditions into regions supersaturated with respect to crystalline phases.

Short-range interactions are calculated with a slightly modified UNIFAC model (Fredenslund et al., 1975) using the revised parameter set of Hansen et al. (1991) for most of the functional group interactions. Modifications of the UNIFAC model part within AIOMFAC include further the introduction of inorganic ions, to account for their effects on the entropy and enthalpy of mixing apart from their charge-related interactions (Li et al., 1994; Yan et al., 1999; Zuend et al., 2008). Owing to the importance of hydroxyl and carboxyl functional groups in organic aerosols, we furthermore use the specific UNIFAC parameterizations of Marcolli and Peter (2005) for alcohols/polyols and the parameterization of Peng et al. (2001) for the COOH group of carboxylic acids, for associated interaction parameters where these improved UNIFAC parameterizations differ from the standard UNIFAC parameterization by Hansen et al. (1991).

Figure 1 shows examples for the assignment of main groups in AIOMFAC. Note that the functional groups of a chemical species are divided into so-called main groups and subgroups according to UNIFAC convention (Fredenslund et al., 1975; Marcolli and Peter, 2005; Zuend et al., 2008). E.g., the alkyl groups CH_3, CH_2, CH and C are different subgroups classified into the main group CH_n. The distinction of different alkyl groups by Marcolli and Peter (2005): $CH_n^{(OH)}$ with an attached OH group, CH_n in hydrophobic tails of alcohols, and CH_n elsewhere in alcohols, is implemented in full detail in the UNIFAC part of AIOMFAC, leading to the significant improvement in the description of interactions of alcohol (and polyol) molecules with themselves and water as described by these authors. However, AIOMFAC main group ↔ ion interactions involving the groups CH_n (in hydrophobic tails of alcohols) and CH_n (in alcohols) are described with the same parameters as CH_n (standard UNIFAC) ↔ ion interactions, as the current database and associated uncertainties do not suggest that a further distinction leads to an overall improvement. With the exception of $CH_n^{(OH)}$ groups, standard UNIFAC CH_n

groups are used for alkyl groups in molecules which contain hydroxyl groups combined with different other functional groups (i.e., non-pure alcohols, see Fig. 1). As intensive testing shows, the consideration of a specific $CH_n^{(OH)}$ group, which accounts for the induced polarity by the neighboring hydroxyl group, leads to a better description of different alcohols, polyols, and sugars within the group-contribution concept. Including the $CH_n^{(OH)}$ group as a distinct functional group in AIOMFAC is justified, since unlike other polar groups, such as COOH or CH_nCO, the OH group does not comprise the CH_n group it is bonded to.

Note that organic acids are treated as undissociated species in AIOMFAC. This is a simplification, as organic acids, e.g., dicarboxylic acids, tend to dissociate at least partially in dilute aqueous solutions. This simplification is justified for moderately to highly concentrated solutions of carboxylic acids and when reactions with strong bases are not considered. The reason for this simplification, and with it the omission of carboxylate ions and salts, is the group-contribution representation. In order to explicitly treat the partial dissociation of organic acids within a group-contribution method, one would need to define a dissociation constant of the carboxyl functional group, but different organic acids have quite different dissociation constants (Clegg and Seinfeld, 2006a,b), making it difficult to assign a specific dissociation constant to the COOH group. Moreover, experimental data to determine interactions between carboxylate anions and inorganic cations are rather incomplete (Clegg and Seinfeld, 2006b). Therefore, we neglect the dissociation of organic acids in aqueous solutions. However, the effects of partially dissociated carboxylic acids on the non-ideal mixing behavior are to some extent implied by means of the ionic strength-dependent COOH $\leftrightarrow$ ion interaction contributions.

All compound-specific parameters in the LR and SR parts are already set and non-adjustable, as described by Zuend et al. (2008). This includes all interactions among different organic compounds and water, which are treated in the modified UNIFAC model that makes up the AIOMFAC SR part. Hence, all adjustable AIOMFAC parameters to optimize the description of organic functional groups $\leftrightarrow$ ion interactions in mixtures are implemented in the MR part. We focus in the following description only on

the new and extended parameterization of the organic main group $\leftrightarrow$ ion interactions to additional functional groups in the MR part, while retaining the AIOMFAC MR-part expressions as given by Zuend et al. (2008) and refer to that previous work for a complete and detailed description of the AIOMFAC model expressions.

The expression for $G_{\text{MR}}^{\text{ex}}$ of a mixture containing n_k moles of solvent main groups k (main groups of organics and water), with molar masses M_k, and n_i moles of ions i is (Zuend et al., 2008):

$$
\begin{aligned}
\frac{G_{\text{MR}}^{\text{ex}}}{RT} &= \frac{1}{\sum_k n_k M_k} \sum_k \sum_i B_{k,i}(I) n_k n_i \\
&+ \frac{1}{\sum_k n_k M_k} \sum_c \sum_a B_{c,a}(I) n_c n_a \\
&+ \frac{1}{\sum_k n_k M_k} \sum_c \sum_a C_{c,a}(I) n_c n_a \sum_i \frac{n_i |z_i|}{\sum_k n_k M_k} \\
&+ \frac{1}{\sum_k n_k M_k} \sum_c \sum_{c' \geq c} R_{c,c'} n_c n_{c'} \\
&+ \frac{1}{\left(\sum_k n_k M_k\right)^2} \sum_c \sum_{c' \geq c} \sum_a Q_{c,c',a} n_c n_{c'} n_a .
\end{aligned}
\tag{4}
$$

Here, n_c and $n_{c'}$ are moles of cations, n_a are moles of anions, and I is the ionic strength on a molal basis: $I = \frac{1}{2} \sum_i m_i z_i^2$, with molalities m_i and integer number of elementary charges z_i of ions i. $B_{k,i}(I)$ and $B_{c,a}(I)$ are ionic strength dependent binary interaction coefficients between solvent main groups and ions, and between cations and anions, respectively. $C_{c,a}(I)$ are interaction coefficients between cation $\leftrightarrow$ anion pairs with respect to the total charge concentration. The coefficients $R_{c,c'}$ and $Q_{c,c',a}$ describe

binary and ternary interactions involving two different cations. These latter two interaction coefficients have been introduced by Zuend et al. (2008) to improve the description of systems containing the ion combinations NH_4^+, H^+ or NH_4^+, H^+, SO_4^{2-} (e.g., aqueous sulfuric acid + ammonium sulfate solutions), especially at very high ionic strength.
5 Hence, the last two terms of Eq. (4) vanish in other cases.

The first three interaction coefficients in Eq. (4) are parameterized as functions of ionic strength I. In AIOMFAC, we use expressions similar to those used for Pitzer models:

$$B_{k,i}(I) = b_{k,i}^{(1)} + b_{k,i}^{(2)} e^{-b_{k,i}^{(3)} \sqrt{I}}, \tag{5}$$

10 $$B_{c,a}(I) = b_{c,a}^{(1)} + b_{c,a}^{(2)} e^{-b_{c,a}^{(3)} \sqrt{I}}, \tag{6}$$

$$C_{c,a}(I) = c_{c,a}^{(1)} e^{-c_{c,a}^{(2)} \sqrt{I}}, \tag{7}$$

where $b_{k,i}^{(1)}$, $b_{k,i}^{(2)}$, $b_{c,a}^{(1)}$, $b_{c,a}^{(2)}$, $b_{c,a}^{(3)}$, $c_{c,a}^{(1)}$, and $c_{c,a}^{(2)}$ are adjustable AIOMFAC parameters. The parameter $b_{c,a}^{(3)}$ has been found to describe most aqueous salt solutions, when assuming a fixed value of $0.8\,\mathrm{kg}^{1/2}\,\mathrm{mol}^{-1/2}$. In cases where this value did not result in a
15 satisfactory data fit, $b_{c,a}^{(3)}$ has been allowed to vary (Zuend et al., 2008). The parameter $b_{k,i}^{(3)}$ is kept constant for all organic-inorganic solutions at a value of $1.2\,\mathrm{kg}^{1/2}\,\mathrm{mol}^{-1/2}$. All interaction coefficients in the MR part are symmetric, i.e. $B_{k,i}(I) = B_{i,k}(I)$. Since water is defined as the reference solvent for inorganic ions, no explicit ion ↔ water interactions are determined, i.e., $B_{k=\mathrm{H_2O},i}(I) = 0$ for all inorganic ions. However, non-
20 ideality effects from cations and anions interacting with water molecules are indirectly accounted for via the cation ↔ anion interaction coefficients, $B_{c,a}(I)$, $C_{c,a}(I)$, $R_{c,c'}$, and $Q_{c,c',a}$, as the corresponding interaction parameters have been determined on the basis of (organic-free) aqueous electrolyte solutions.

In this study, the organic main group ↔ ion interaction parameters $b_{k,i}^{(1)}$ and $b_{k,i}^{(2)}$ of
25 the $B_{k,i}(I)$ coefficients (Eq. 5) are revised or determined for the first time. In addition,

we revise the MR parameters involved in aqueous ammonium sulfate + sulfuric acid mixtures (to correct for an error in the previous parameter estimation, see Sect. 5.1) and we fitted the parameters of Eqs. (6) and (7) for $Mg^{2+} \leftrightarrow Br^-$, $Ca^{2+} \leftrightarrow Br^-$, and $Ca^{2+} \leftrightarrow SO_4^{2-}$ interactions. All other model parameters are kept as given in Zuend et al. (2008).

3.2 Uncertainty and the determination of model parameters

The adequate consideration of uncertainties in both experimental data and the model is crucial for the determination of organic main group $\leftrightarrow$ ion interaction parameters. Qualitatively, an organic + water + salt system can be modeled in terms of organic $\leftrightarrow$ organic, organic $\leftrightarrow$ water, organic $\leftrightarrow$ ion, and aqueous cation $\leftrightarrow$ anion interactions (cation $\leftrightarrow$ cation and anion $\leftrightarrow$ anion interactions can usually be neglected, see description of Eq. (4) for exceptions). In the group-contribution framework of AIOMFAC (and UNIFAC), organic $\leftrightarrow$ organic interactions are implemented on the level of interactions between organic functional groups (subgroups/main groups in UNIFAC part), while organic $\leftrightarrow$ ion interactions are described by organic main groups interacting with inorganic ions (no distinction on subgroup level as in LIFAC, Yan et al., 1999; Kiepe et al., 2006). Model uncertainties are associated with each of these types of interactions. Moreover, each measured quantity has its own level of random and systematic errors, which also depend on mixture composition, rendering some data points more reliable than others. This needs to be considered during the parameter determination procedure, e.g., by applying a meaningful weighting procedure to the individual datasets.

In order to parameterize organic $\leftrightarrow$ ion interactions from measurements, the deviations between measured thermodynamic equilibrium quantities and corresponding calculated quantities can be minimized by improving the organic $\leftrightarrow$ ion interaction parameters, provided that the contributions from all other binary interactions are already correctly considered. However, if there are significant uncertainties and corresponding deviations caused by other interaction contributions, the deviations between measured

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and calculated quantities cannot be attributed entirely to the organic ↔ ion interaction. Zuend et al. (2008) showed that activity coefficients in aqueous electrolyte solutions are accurately calculated by AIOMFAC, so that it is justified to assume uncertainties from aqueous cation ↔ anion interactions to be negligible. Inherent to the group-contribution concept, organic ↔ water and organic ↔ organic contributions from the UNIFAC model part bear higher uncertainties, as can be seen from comparisons of UNIFAC calculations and measurements for salt-free systems. A reduction of the influence of random and systematic errors can be achieved by basing the parameterization on a wide range of data, including different data types and different organic compounds. Preprocessing of some experimental data types in order to isolate the salt-effect on the organics from other contributions, as described in Sect. 4, helps to avoid that deviations arising from limitations of the UNIFAC part are erroneously compensated by organic-inorganic interactions.

Experimental data are not evenly available over all systems of interest. For example, to determine the model parameters for the COOH ↔ Cl$^-$ interaction, ternary datasets of the type "carboxylic acid + water + chloride salt", covering a wide range of different cations are ideally needed for optimum separation of organic ↔ anion interactions. Yet our database contains many more datasets in which the chloride salt is NaCl as compared to NH$_4$Cl (for describing this specific interaction). Hence, the determined COOH ↔ Cl$^-$ interaction parameters might be biased towards NaCl-systems. Another effect, inherent to the group-contribution concept, might interfere: when the ternary systems from the example mentioned above are dominated by propanoic acid (CH$_3$CH$_2$COOH) as the carboxylic acid, which is composed of two CH$_n$ main groups in addition to the carboxyl group, the COOH ↔ Cl$^-$ interaction parameters tend to become biased towards systems with a CH$_n$: COOH ratio of 2 : 1, although the CH$_n$ ↔ Cl$^-$ interaction contribution should not be reflected by the COOH ↔ Cl$^-$ interaction parameters. Furthermore, if only a certain type of data is available to determine a specific organic-inorganic interaction, e.g., experimental water activities, it might not be sufficient to constrain model parameters for accurate predictions of activities of all components. In

general, such issues emerge from the representation of systems and components in AIOMFAC (or any other group-contribution model) and the amount and distribution of datasets used for the model parameter determination.

Although it cannot be completely avoided that an uneven distribution of datasets biases the model parameterization, a database containing a large variety of different datasets for the description of all the binary organic main group ↔ ion interactions is the key to reduce parameterization interferences. This emphasizes the necessity and advantage of fitting all binary interaction parameters simultaneously using the entire database, since all systems are coupled by common ions and/or organic main groups. Provided a sufficient amount of experimental data for different systems exists, covering a wide range of concentrations, the diverse effects arising from organic main group ↔ ion interactions can be disentangled by the parameter optimization procedure.

3.3 Objective function

Finding optimal organic ↔ ion interaction parameters is a challenging multidimensional global optimization problem. In due consideration of the various aspects of model and measurement uncertainties and to enable intercomparability of different quantities, we formulate the following general objective function, subject to minimization:

$$F_{\text{obj}} = \sum_d \sum_u w_{d,u} \left[\frac{Q_{d,u}^{\text{calc}} - Q_{d,u}^{\text{ref}}}{\left| Q_{d,u}^{\text{ref}} \right| + Q_{d,u}^{\text{tol}}} \right]^2 . \tag{8}$$

Here, d is a dataset index, u denotes a point in the dataset, $w_{d,u}$ is the weighting of a data point as calculated from Eq. (9), and the sums cover all data points in all datasets considered. $Q_{d,u}^{\text{ref}}$ is a given reference quantity, i.e., a measured value or a quantity derived from measurements by means of thermodynamic relations. $Q_{d,u}^{\text{calc}}$ is the corresponding quantity calculated with the model at given conditions. $Q_{d,u}^{\text{tol}}$ is a tolerance quantity (> 0) with the same units as $Q_{d,u}^{\text{ref}}$, representing the measurement

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uncertainty or model sensitivity as described below. The range of values and units of the actual quantities depend on the data type (data types are discussed in Sect. 4). To simplify the procedure of assigning individual weightings to data points based on the data type and other properties, such as the number of data points in a dataset, N_d, the following approach is used:

$$
w_{d,u} = \begin{cases} w_d^{\text{init}} & \text{if } N_d \leq \eta, \\ w_d^{\text{init}} \times \frac{\eta}{N_d} & \text{if } N_d > \eta, \end{cases} \tag{9}
$$

where w_d^{init} is an initial weighting assigned to dataset d, considering only its type and temperature range, assuming the number of data points to be η, regardless of the actual number (N_d). Here we set $\eta = 10$, which is a characteristic number of points of the datasets considered. Equation (9) reduces the influence of datasets containing a large number of points, while avoiding an inordinately large weighting of datasets with only very few points. Initial weightings assigned to the datasets for the model fit are given in Table 2.

In case $Q_{d,u}^{\text{ref}}$ is an experimentally determined value, such as a ternary mixture composition at salt saturation or the relative humidity in equilibrium with a bulk solution (i.e., the water activity), the corresponding tolerance quantity, $Q_{d,u}^{\text{tol}}$, can be considered a characteristic uncertainty of the measurement. $Q_{d,u}^{\text{tol}}$ would then be a stated measurement error or the standard deviation of several repeated experiments. However, for most of the data considered in the model fit, error bars are not given. Furthermore, we would like to know the sensitivity of activity coefficients with respect to a stated or assumed experimental uncertainty. Common to all measurements is the possibility of a slight error in composition. Therefore, we use the AIOMFAC model to calculate the effect of a tiny change in composition on the activity coefficients of the different mixture components by means of a total molar derivative:

$$
s_t^\gamma(x^*) = dn^{\text{tol}} \left(\left| \frac{\partial \gamma_t}{\partial n_1} \right|_{T, n_j \neq n_1} + \left| \frac{\partial \gamma_t}{\partial n_2} \right|_{T, n_j \neq n_2} + \ldots + \left| \frac{\partial \gamma_t}{\partial n_k} \right|_{T, n_j \neq n_k} \right). \tag{10}
$$

Here, $s_t^\gamma(x^\star)$ is the activity coefficient sensitivity of component t at a composition $x^\star(x_1, x_2, \ldots, x_k)$ of a k-component system and dn^{tol} is a molar increment corresponding to a mole fraction tolerance x^{tol} characteristic for the dataset ($dn^{tol} = x^{tol} \times 1\,mol$). In this study, we chose $x^{tol} = 0.01$ for all datasets, which we consider a reasonable error tolerance for the use with a group-contribution model. The partial derivatives of γ_t are calculated with respect to a molar change of each independent mixture component $(n_1, \ldots, n_k)$, while keeping the molar amounts n_j of all other components fixed at the values corresponding to $x^\star$. Similarly, replacing the activity coefficient by the activity a_t of a component in Eq. (10), the activity sensitivity $s_t^a(x^\star)$ is calculated. The sensitivity $s_t^\gamma(x^\star)$ provides a measure of the extent to which calculated AIOMFAC activity coefficients are sensitive to an error in a given mixture composition. If the relationship between a mixture composition and associated activity coefficients is experimentally determined to some degree of certainty and found to be sufficiently well represented by AIOMFAC, the calculated activity coefficient sensitivity can also be used to assess the quality of experimental data. Therefore, this concept enables an estimate of composition-related uncertainties of measurements and, thus, a way to determine how much one can trust a certain data point relative to other points/measurements. Other sources of error, more related to the accuracy of a specific experimental technique, can be factored in via the initial dataset weighting. For data types in which the $Q_{d,u}^{ref}$ are activity coefficients or activities, AIOMFAC sensitivities are used to calculate the tolerance quantity of a specific data point required for the objective function computation. For example, if $Q_{d,u}^{ref}$ and $Q_{d,u}^{calc}$ are measured and calculated water activities at composition $x^\star$, then $Q_{d,u}^{tol} = s_w^a(x^\star)$. In other cases, e.g., when $Q_{d,u}^{ref}$ and $Q_{d,u}^{calc}$ are measured and calculated compositions in mole fractions, $Q_{d,u}^{tol}$ is simply: $Q_{d,u}^{tol} = x^{tol}$.

Due to the fact that we use AIOMFAC to compute the sensitivities with a certain test set of interaction parameters at each iteration step (F_{obj} evaluation) during the parameter optimization procedure, the sensitivities calculated from Eq. (10) are a result of the AIOMFAC test-parameterization that feeds back on the objective function
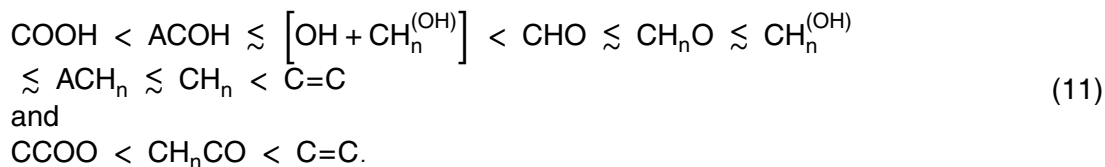
value. Hence, in principle there are two options to minimize F_{obj}: (1) by minimizing the numerator $(Q_{d,u}^{calc} - Q_{d,u}^{ref})^2$, which is desired, or (2) by maximizing the denominator (at a suboptimal nominator) via maximizing $Q_{d,u}^{tol}$, which should be avoided. In practice, feedback loops maximizing $Q_{d,u}^{tol}$ during parameter optimization do not pose a problem,

5 because $Q_{d,u}^{tol}$ depends only on the sensitivities for certain data types. Data distributed over a wide concentration range automatically corrects a tendency for option (2). The denominator of Eq. (8) is also designed to restrict the influence of data points with a very low sensitivity by the additional term $Q_{d,u}^{ref}$. Data with a very low activity coefficient sensitivity are typically rather insensitive to organic main group ↔ ion interactions, e.g.,

10 water activity at high mole fractions of water, and a high weighting of such data would only add more noise instead of signal to the actual parameter optimization problem.

3.4 Constraints based on functional group polarity series

The physicochemical meaning of the binary interaction coefficients $B_{k,i}(I)$ provides additional information to constrain the parameters $b_{k,i}^{(1)}$ and $b_{k,i}^{(2)}$ to a meaningful range.

15 The first term on the right-hand side of Eq. (4) (which includes $B_{k,i}(I)$) represents contributions to the Gibbs excess energy attributed to two-body interactions between organic main groups and ions. While the contribution of this term scales with the molalities of involved organic main groups and ions, the interaction coefficients $B_{k,i}(I)$ are functions of ionic strength only. These coefficients represent interaction strengths, specific to

20 each main group-ion pair. However, relative to the same ion i^* at a given ionic strength I°, we argue that the different $B_{k,i^*}(I^\circ)$ values are not independent of each other, but rather that they are related to each other and depend on the polarity of the main groups k. Ions have a higher affinity for polar functional groups than for nonpolar groups due to charge ↔ permanent dipole interactions with polar functional groups. Additionally, the

25 polar carboxyl group partially dissociates in dilute solutions, enabling charge ↔ charge interactions and certain ions, e.g., NO_3^- and SO_4^{2-}, can also form hydrogen bonds with

hydroxyl and carboxyl groups, which can lead to salting-in of organic compounds. On the other hand, much weaker (attractive) interactions between ions and nonpolar main groups are the main cause for the salting-out effect of ions on organics in aqueous solutions. Here, the reference value for $B_{k,i}(I^\circ)$ is the interaction with water, for which we have $B_{H_2O,i}(I^\circ) = 0$ (by definition). Therefore, in the case of nonpolar main groups, the $B_{k,i}(I^\circ)$ values are expected to be positive and greater than the $B_{k,i}(I^\circ)$ of polar main groups, representing the larger difference of nonpolar group $\leftrightarrow$ ion interactions relative to interactions of ions with polar water molecules. We formulate a functional group polarity series for the interaction coefficient $B_{k,i}(I^\circ)$ with the polarity of main groups k in decreasing order:

$$
\begin{aligned}
&\text{COOH} < \text{ACOH} \lesssim \left[\text{OH} + \text{CH}_n^{(OH)} \right] < \text{CHO} \lesssim \text{CH}_n\text{O} \lesssim \text{CH}_n^{(OH)} \\
&\lesssim \text{ACH}_n \lesssim \text{CH}_n < \text{C=C} \\
&\text{and} \\
&\text{CCOO} < \text{CH}_n\text{CO} < \text{C=C}.
\end{aligned}
\tag{11}
$$

The inequality signs are with respect to the values of $B_{k,i}(I^\circ)$. The decrease in polarity of this series is parallel to the decrease in the oxygen-to-carbon ratio (O : C) of the main groups. Note that the groups CCOO, CH_nCO, and C=C are distinct from the other functional groups in that they consist of two carbon atoms and therefore need to be considered in a separate series. However, in terms of their Gibbs energy contributions according to Eq. (4), these functional groups can be thought of as units consisting of two single carbon-containing groups, e.g., $\text{CH}_n\text{CO} \approx \text{CH}_n + \text{CHO}$ or C=C $\approx \text{CH}_n + \text{CH}_n$. Hence, the second series of Relation (11) is, within a certain tolerance, related to the first series. Relation (11) allows one to formulate a set of inequality expressions, e.g.: $B_{COOH,i}(I^\circ) < B_{ACOH,i}(I^\circ)$, $B_{CH_nO,i}(I^\circ) < B_{CH_n,i}(I^\circ)$, $B_{CH_nCO,i}(I^\circ) < B_{C=C,i}(I^\circ)$, etc. Such inequality expressions are used as additional constraints during the determination of the model parameters by evaluating $B_{k,i}(I^\circ)$ at $I^\circ = 0.001\,\text{mol}\,\text{kg}^{-1}$, $0.1\,\text{mol}\,\text{kg}^{-1}$, $10\,\text{mol}\,\text{kg}^{-1}$, and $100\,\text{mol}\,\text{kg}^{-1}$. These constraints effectively restrict the

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parameter range for each main group-ion pair. Among the advantages of such an approach are the resulting physically meaningful $B_{k,i}(I)$ interaction contributions and, with regard to predictions (extrapolations) on the basis of the group-contribution concept, a more reliable parameterization of AIOMFAC.

4 Types and processing of experimental data

Central for a reliable parameterization of AIOMFAC is a broad distribution of experimental data, comprising mixtures containing the target functional groups and inorganic ions at various concentrations. The theoretical basis common to different experimental techniques and data types is thermodynamic equilibrium. Equilibria between the gas phase and a liquid mixture constitute the basis for vapor-liquid equilibrium (VLE) phase composition measurements, equilibria between coexisting liquid phases provide liquid-liquid equilibrium (LLE) tie-line data, and equilibria between solid and liquid phases (SLE) furnish composition data of saturated solutions. Measurements of the electrical conductivity in electrolyte solutions relative to a standard cell potential, so called electromotive force (EMF) measurements, allow a direct determination of mean molal activity coefficients.

The relatively weak temperature dependence of activity coefficients allows the use of data measured at somewhat higher or lower temperatures than 298 K. In this respect, dataset weightings are also used to account for a temperature effect, assigning higher weightings to datasets closer to 298 K. In the following, the different data types, their processing and use in the model parameterization are described.

4.1 Vapor-liquid equilibrium data

VLE data comprise the mole fraction composition of the gas phase (y) and the liquid mixture (x) under isothermal or isobaric conditions (x-y-T-p VLE data). Isobaric measurements are typically conducted at 1 atm pressure (101 325 Pa), by measuring the

boiling point temperature of different mixture compositions. Therefore, such measurements report data at higher temperatures. Almost all VLE data considered are ternary organic + water + salt mixtures, in which the salt is present only in the liquid phase. Treating the gas phase as an ideal gas mixture, activity coefficients of the organic component and water can be obtained from modified Raoult's law:

$$\gamma_j^{(x)} = \frac{p_j}{p_j^\circ x_j}. \tag{12}$$

Here, p_j is the partial pressure of the semivolatile component j, given from $p_j = y_j p$, where y_j is the measured gas-phase mole fraction at total system pressure p. $p_j^\circ(T)$ is the pure liquid compound saturation vapor pressure and x_j the liquid-phase mole fraction, defined on the basis of the completely dissociated salt: $x_j = n_j / (\sum_s n_s + \sum_i n_i)$, where n_s are moles of solvent species (organics, water) and n_i are moles of the different ions. Saturation vapor pressures of organics and water at different temperatures are calculated using the Antoine equation with coefficients from the Landolt-Börnstein database (Dykyj et al., 2000). With the exception of carboxylic acids, the assumption of an ideal gas mixture is well justified for the pressure and temperature range of the data. Tests with gas-phase fugacity corrections show a negligible effect on $\gamma_j^{(x)}$ – partly since the ratio p_j/p_j° moderates real-gas behavior. Gas-phase association of carboxylic acids, such as formic, acetic, and propanoic acids, is accounted for by the relations of Chueh (1974) with dimerization equilibrium coefficients from Tsonopoulos and Prausnitz (1970). The availability of VLE measurements for salt-free organic + water systems at similar conditions allows a further processing of activity coefficients with the goal to isolate the salt-effect on the organics from other contributions. Isolating the salt-effect enables achieving qualitative agreement of model and experimental data in terms of salting-in or salting-out effects of a certain electrolyte on an organic compound. This is useful since at lower salt concentrations uncertainties in the UNIFAC part of AIOMFAC might lead to a qualitatively wrong parameter fitting, i.e., forcing the model towards predicting a salting-in effect when salting-out is actually observed. The idea of isolating

the salt-effect is to calculate the deviation $\Delta^{sc,sf}\gamma_j^{(x)}(x_j')$ of a component's activity coefficient in the salt-containing (sc) from the corresponding salt-free (sf) system, calculated at the same liquid mixture mole fraction x_j' (superscript ′ denotes here the calculation of mole fractions on a salt-free basis, i.e., even when a salt is present in the mixture) and temperature range:

$$\Delta^{sc,sf}\gamma_j^{(x)}(x_j') = \gamma_j^{(x),sc}(x_j') - \gamma_j^{(x),sf}(x_j'). \tag{13}$$

To compute activity coefficients in salt-free systems at exactly the same x_j' as given from the salt-containing VLE data, we use a molar Gibbs excess energy parameterization, fitted to VLE data of salt-free systems, preferentially measured by the same groups/experimental setups that also report the salt-containing datasets. Following McGlashan (1963), we formulate a 4th-order molar Gibbs excess energy series parameterization satisfying the Gibbs-Duhem-Margules relation for binary systems (McGlashan, 1963; Soonsin et al., 2010):

$$\frac{g^{ex}}{RT} = x_2(1-x_2) + \left[\sum_{i=1}^{k} c_i(1-2x_2)^{i-1}\right], \tag{14}$$

$$\frac{d\left[g^{ex}/(RT)\right]}{dx_2} = (1-2x_2) + \left[\sum_{i=1}^{k} c_i(1-2x_2)^{i-1}\right]$$

$$+ x_2(1-x_2)\left[-2\sum_{i=2}^{k}(i-1)c_i(1-2x_2)^{i-2}\right], \tag{15}$$

$$\ln\gamma_2^{(x)} = \frac{g^{ex}}{RT} + (1-x_2)\frac{d\left[g^{ex}/(RT)\right]}{dx_2}, \tag{16}$$

$$\ln\gamma_1^{(x)} = \frac{g^{ex}}{RT} - x_2\frac{d\left[g^{ex}/(RT)\right]}{dx_2}, \tag{17}$$

Extended parameterization of the AIOMFAC model

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where g^{ex} is the molar Gibbs excess energy of a binary solution (components 1 and 2) and c_i ($i = 1, \ldots, k$) are fitted, system-specific coefficients up to order $k = 4$, given in Table 1. Equations (16) and (17) provide then the $\gamma_j^{(x),sf}$ required in Eq. (13). The data processing with Eq. (13) leads in most cases to a clear qualitative and quantitative distinction between the salt-effect on water (predominately salting-in) and on organic compounds (predominately salting-out).

For complete (x-y-T-p) VLE datasets, Eq. (13) is used to define the reference quantity, $Q_{d,u}^{ref} = \Delta^{sc,sf}\gamma_j^{(x)}$. $Q_{d,u}^{calc}$ is calculated accordingly by the model. $Q_{d,u}^{tol}$ is defined using the model sensitivity of the activity coefficient deviation as $Q_{d,u}^{tol} = s_t^\gamma (\Delta^{sc,sf}\gamma_j^{(x)}) + 1$, where the term $+1$ ($= \gamma_j^{(x),ideal}$) attenuates effects from noisy data on the special salt-effect isolation treatment (when introduced in the denominator of Eq. 8). An example of the use of VLE data processed this way is shown in Fig. 2 for the ternary system water + 2-propanol + LiCl. This system is representative for the behavior of many ternary VLE systems in that it shows a strong salting-out effect on the organic, i.e., large positive deviations from the electrolyte-free baseline (where $\Delta^{sc,sf}\gamma_{org}^{(x)} = 0$), at compositions where the organic component makes up only a small fraction of the solution and the electrolyte concentration is relatively high. This enhanced salting-out effect can be intuitively explained by the microscopic view that at such conditions, moderating organic ↔ organic interactions are largely diminished, whereas organic ↔ ion interactions are more frequent, due to the higher probabilities of an organic molecule to directly interact with an ion (or with a water molecule), than with another organic molecule. Typical for such electrolyte-containing mixtures, dilute with respect to the organic fraction, is an increased model sensitivity to small variations in composition, which explains and justifies an increase in the deviations between calculated and measured activity coefficients of the organic compound.

Some VLE datasets are incomplete in the sense that they provide only, e.g., x-y-T data, where total pressure information is missing. In such cases, the gas-phase mole fraction y_1 is used as a reference quantity and corresponding values are calculated

with AIOMFAC.

4.2 Water activity data

A special case of VLE data are water activities a_w of bulk solutions or from aqueous droplets. The latter are typically investigated in an electrodynamic balance (EDB), with a hygroscopicity tandem differential mobility analyzer (HTDMA), or by micro-Raman spectroscopy. In bulk experiments, the (water) vapor pressure or relative humidity (RH) of the gas phase in equilibrium with a solution of a given composition is measured. Solution concentrations up to saturation can be reached. In EDB, HTDMA or micro-Raman measurements, droplets are equilibrated in an atmosphere of known RH. The radius or volume change of the droplets reflects the water uptake or release as a function of RH and can be related to absolute water content when the dry mass is known or when bulk reference water activities at high RH are available. EDB and HTDMA measurements are usually less accurate than bulk measurements because of uncertainties in both, ambient RH and water content. However, they can access the supersaturated concentration range because small droplets with little contact to surfaces can reach high supersaturations. Accurate water activity measurements of bulk solutions and droplets require the vapor pressure of the organic component to be low with respect to the water vapor pressure. Water activity measurements have the advantage of providing data at room (or even lower) temperatures and are a useful data source to constrain organic ↔ ion interactions, although water activities are only indirectly affected by such interactions (Gibbs-Duhem relation). In case of a_w data, $Q_{d,u}^{ref}$ and $Q_{d,u}^{calc}$ are the measured and calculated $a_w^{(x)}$ values at given mixture compositions and $Q_{d,u}^{tol}$ are the calculated water activity sensitivities (Eq. 10). Figure 3 shows measured and calculated water activities in the system water + malonic acid + $(NH_4)_2SO_4$ at 298 K. The deviations of water activities in the ternary mixtures as compared to a_w of the salt-free water + malonic acid system represent the effects of water ↔ ion and malonic acid ↔ ion interactions (here the ions are NH_4^+ and SO_4^{2-}). In this example,

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measured water activities are relatively well represented by the AIOMFAC calculations, with slightly higher deviations at lower water contents. The many data points in this dataset, with compositions covering a variety of malonic acid : ammonium sulfate ratios, are one way to facilitate that the model parameter optimization is not biased towards a specific organic : inorganic mixing ratio.

4.3 Liquid-liquid equilibrium data

The type of LLE data that is useful for the AIOMFAC parameterization are so-called tie-line measurements, where the compositions of two coexisting liquid phases at a certain temperature are determined. One way to compare AIOMFAC predictions with experimental data, is to perform a liquid-liquid phase separation computation, for which an initial mixture composition of the experimental tie-line is needed as input. To do this, we use the computation method for liquid-liquid phase separation described by Zuend et al. (2010), using AIOMFAC for the Gibbs energy calculation. An initial mixture composition, with mole fractions x_j^{init}, on an unstable/metastable point on a tie-line is generated by

$$x_j^{\text{init}} = \frac{1}{2}\left(x_j^{\alpha} + x_j^{\beta}\right),\tag{18}$$

where x_j^{α} and x_j^{β} are the experimentally determined compositions of the two liquid phases, α and β, at equilibrium. This way, measured and calculated phase compositions can be directly compared. However, this approach unfortunately involves high computational costs that cannot be avoided when a reliable detection of the LLE composition is essential. Such computational demands are acceptable when only a few LLE data points are used with a small number of fit parameters. In this study, where thousands of LLE data points are used and ∼250 parameters need to be determined simultaneously, taking up to a million objective function evaluations including billions of AIOMFAC calls – the described LLE prediction approach is simply unfeasible. Thus, a different, computationally more efficient use of LLE data is mandatory.

To overcome this technical barrier, we make use of the thermodynamic phase equilibrium conditions. Based on the reference state definitions of AIOMFAC, activities of the different independent components have to be equal in coexisting phases, i.e., $a_s^{(x),\alpha} = a_s^{(x),\beta}$ in case of solvent components and $\text{IAP}_{MX}^{\alpha} = \text{IAP}_{MX}^{\beta}$ in case of electrolytes,

5   where

$$\text{IAP}_{MX} = \left(a_M^{(m)} \right)^{\nu^+} \times \left(a_X^{(m)} \right)^{\nu^-} \tag{19}$$

is the molal ion activity product of electrolyte unit "$M_{\nu^+} X_{\nu^-}$" with ν^+ cations M and ν^- anions X (Zuend et al., 2010). This isoactivity condition enables a direct calculation and comparison of activities in coexisting phases at the experimental LLE compositions.

10   Typical for organic + water + salt LLE is that only a very small amount of electrolyte is dissolved in the organic-rich phase and only a small part of the organic fraction is present in the aqueous-electrolyte phase. This makes the sensitivity to small errors in phase composition very high, because tiny amounts of electrolyte need to be detected accurately in a predominantly aqueous-organic phase. Moreover, the activity sensitivi-

15   ties of electrolytes and organics in their respective concentration-poor phases are very high. Therefore, a good choice for $Q_{d,u}^{\text{ref}}$ and especially the consideration of the sensitivities by $Q_{d,u}^{\text{tol}}$ is of crucial importance. The objective function terms of LLE data are therefore defined in a dataset- and component-specific manner. For each component in a dataset d, the phase in which the activity sensitivity s_j^a is smaller on average, is

20   defined as the reference phase, which is typically the phase where j is enriched. At a data point u, $Q_{d,u}^{\text{ref}}$ of a component j is then set to the activity value (IAP in case of electrolytes) of j in the reference phase. The tolerance quantity is defined as the sum of the activity sensitivities from both phases: $Q_{d,u}^{\text{tol}} = s_j^{a,\alpha} + s_j^{a,\beta}$. Figure 4 shows such LLE rel. activity deviations for tie-line data of the quaternary system water + 4-

25   methyl-2-pentanone + acetic acid + NaCl at 308 K. The absolute values of the relative activity deviations as plotted in Fig. 4 are calculated relative to the compound-specific reference phase activities plus activity sensitivities, analogously to the calculation of

their contributions to F_{obj}. In these kind of LLE data representations, a value of | rel. activity deviation | < 0.2 can be considered relatively "good". Figure 4 reveals that components which predominately partition to one of the liquid phases, i.e., electrolytes and hydrophobic organics, typically show higher sensitivity to small composition changes than components more abundant in both phases, as e.g., water. The reasons for this behavior are analogous to the ones discussed above in case of VLE data.

The described isoactivity condition method is computationally efficient and enables an alternative way to use LLE data for the model parameter determination. For plots and evaluation of calculated and experimental ternary LLE data, we use the LLE phase separation computation approach as well, enabling a direct comparison of predicted and experimentally determined phase compositions. An example of this is shown in Fig. 5 for the ternary system water + *tert*-butanol + NaCl at 298 K. Panel (a) of Fig. 5 shows the miscibility gap mapped on a coordinate system that depicts the water contents of the two phases as a function of the water-free "dry" composition. Panel (b) shows the same system on a coordinate system that emphasizes the very different contents of *tert*-butanol and NaCl in the two phases. The phase separation computation using AIOMFAC predicts a slightly wider miscibility gap, but is in general agreement with the measurements.

4.4 Solid-liquid equilibrium data

Solid-liquid equilibria constitute mixture composition data, at which liquid mixtures are in equilibrium with a solid phase. In the case of binary systems at isothermal conditions, there is only one specific SLE-composition point, e.g., the saturated solution of a salt in water at 298 K (at a salt-specific equilibrium deliquescence relative humidity). For ternary systems at constant temperature, SLE data define a solubility limit curve of points at different mixture compositions. In case of ternary aqueous organic-inorganic systems, the salt, water or the organic compound can form crystalline solids, depending on the mixture composition and temperature. Solid-liquid equilibria can become complicated when hydrates or mixed crystals form. Thermodynamic equilibrium

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conditions require all solution components, present in the solid phase, to hold a specific liquid phase activity, or activity product (in case of salts, hydrates and mixed crystals) at different solution compositions in equilibrium with the same solid phase. For example, a ternary system of 2-ethoxyethanol + water + KCl in SLE with solid KCl, shown in Fig. 6, requires a constant molal ion activity product $IAP_{KCl} = K_{sp}(T)$ at different compositions. A reference value for the solubility product $K_{sp}(T)$ can be calculated with AIOMFAC from the solubility limit in the corresponding binary aqueous system (in this example, water + KCl). Hence, the following information is needed for the use of SLE data: mixture compositions at solubility limit, temperature, and composition of the solid phase.

In order to compare measured with calculated isothermal SLE data, AIOMFAC is used to calculate mixture compositions that fulfill the solubility limit equilibrium conditions. For the following description of our method, let us assume for that a salt MX forms the solid phase. First, the solubility product $K_{sp}(T)$ at the solubility limit of MX is calculated from binary aqueous composition data. Second, at a given ternary composition the salt-free mole fraction composition, $x'_{j,j\neq MX}$, is kept constant, while the molar content of MX with respect to 1 mol total solution is varied (thus changing the mole fractions of all components), until the composition is found, at which the condition $IAP_{KCl} = K_{sp}(T)$ is fulfilled. This is numerically solved by using a root bracketing algorithm (starting at the experimental composition), followed by a few bisection steps, and a modification of Powell's hybrid method (Moré et al., 1980, 1984) to find the root of $IAP_{KCl} - K_{sp}(T) = 0$ efficiently. If the solid phase is an organic, an analogous procedure is used, by keeping the organic-free mole fraction composition constant and varying the organic amount. Therefore, in case of SLE data, $Q_{d,u}^{ref}$ is the experimentally determined composition in mole fractions, $Q_{d,u}^{calc}$ the corresponding mole fractions calculated with AIOMFAC as described above, and $Q_{d,u}^{tol} = x^{tol} (= 0.01)$.

Some datasets state the solubility limit of an organic compound in aqueous electrolyte solutions that are in equilibrium with an organic-rich liquid phase (e.g., Segatin and Klofutar, 2000). If the condition is true, that virtually no electrolyte is present in the

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organic-rich liquid phase, such ternary LLE-solubility data can be used analogously to SLE solubility data. This condition is fulfilled only in the case of rather hydrophobic organic compounds, which also exhibit limited solubility in pure water.

4.5 Electromotive force data

In EMF measurements, the electric potential difference between two different electrodes in an electrolyte solution (galvanic cell) is recorded as a function of pressure, temperature, and solution composition. Using the modified Nernst equation and a system-specific activity coefficient model, such as a Pitzer model, mean molal activity coefficients $\gamma_\pm$ can be calculated from the EMF data at different electrolyte molalities (e.g., Robinson and Stokes, 2002; Roy et al., 1972a; Esteso et al., 1989). Mean molal activity coefficients from EMF data are derived with the reference state of an infinitely dilute electrolyte solution in the corresponding solvent mixture, while the reference state of electrolytes in AIOMFAC is the infinitely dilute solution in pure water. Hence, to correctly use such EMF $\gamma_\pm$ data, we run AIOMFAC in a mode that also refers to the aqueous-organic solvent mixture as reference state. Figure 7 shows such $\gamma_\pm$ data and associated model sensitivities for the system water + ethanol + KCl. In case of EMF data, $Q_{d,u}^{\text{ref}}$ and $Q_{d,u}^{\text{calc}}$ are measured and calculated $\gamma_\pm$ on molal solvent mixture reference state basis and $Q_{d,u}^{\text{tol}}$ is the corresponding $\gamma_\pm$ sensitivity, $s^{\gamma_\pm}$.

4.6 Database overview

The nature of the group-contribution concept requires the use of several organic compounds, representing combinations of functional groups in different ratios, to unambiguously attribute interaction contributions to each main group ↔ ion pair, as discussed in Sect. 3.2. We therefore carried out an extensive literature search to establish the AIOMFAC parameterization database, covering experimental datasets published in the time period from 1896 to 2010. This included the laborious task of converting many different kinds of concentration scales that have been used by the authors to report

their measurements into a consistent set of input data for AIOMFAC. We furthermore conducted selected water activity and solubility measurements to complement the literature data. Tables reporting our own measurements and a brief discussion of the experimental methods are presented in Appendix A2.

An overview of the database is given in Table 2, listing for all datasets the corresponding system components and main groups, data type, temperature range of the measurements, number of data points, the assigned initial weighting used in the model fit, and the data source. Overall, the database contains more than 450 different datasets totaling ~10 000 data points, covering 12 different inorganic ions and more than 90 different organic compounds composed of 11 different organic main groups. Table 3 presents selected properties of the organic compounds and their structural representation in terms of UNIFAC/AIOMFAC subgroups.

Figure 8 summarizes the database in terms of number of datasets per main group ↔ ion interaction pair. The number of different datasets per interaction pair serves as a qualitative estimate of the degree of confidence that can be expected for a certain interaction parameter, shown by the coloring in Fig. 8. Of course, factors like the composition range, experimental and model uncertainties, and counterions and main groups present in a mixture also influence how well a certain main group ↔ ion interaction pair is constrained by the available data. In a best case scenario, a single dataset covering a wide composition range can be sufficient to constrain a certain main group ↔ ion interaction parameter, if all other main groups and the counterion present in the mixture are well constrained by other data. Compared to that, in other cases, several similar datasets, covering only a limited composition range, might not reach the same degree of confidence associated with determined interaction parameters, albeit the higher number of datasets.

Apparent gaps and deficiencies in the database concerning the coverage of main group ↔ ion interaction pairs are due to the lack of experimental data for systems including those interactions. Especially for some of the interactions involving inorganic acids and bromides, this lack of data is explained by the difficulty of conducting

experiments with systems in which components may chemically react, e.g., hydration reaction of aldehydes or oxidation of aldehydes in Br$^-$ containing solutions.

A relatively high number of datasets contain Na$^+$ and/or Cl$^-$ ions, and NaCl is one of the most abundant salts throughout the database. This reflects the importance of NaCl and other chlorides in chemical process engineering and industrial applications of VLE and LLE for mixture separation purposes, for which many experimental studies have been conducted. From a practical viewpoint regarding new measurements supporting the AIOMFAC parameterization, NaCl can be considered a reference electrolyte and further measurements can be linked to the well-established main group ↔ Na$^+$/Cl$^-$ interaction contributions by using different counterions combined with Na$^+$ or Cl$^-$ in otherwise identical systems. This way, the AIOMFAC model can be extended in the future without the necessity for a simultaneous fit of all interaction parameters.

5 Results and Discussion

5.1 New and revised aqueous electrolyte systems

CaBr$_2$, MgBr$_2$, and CaSO$_4$

Zuend et al. (2008) did not determine all bromide interaction parameters in the original AIOMFAC model. Here we consider the binary bromide systems water + CaBr$_2$ and water + MgBr$_2$ and the sulfate system water + CaSO$_4$. In order to complete the parameter matrix in this respect, we determined the cation ↔ anion interaction parameters $b_{c,a}^{(1)}$, $b_{c,a}^{(2)}$, $b_{c,a}^{(3)}$, $c_{c,a}^{(1)}$, and $c_{c,a}^{(2)}$ for these systems using the experimental datasets listed in Table 4. Resulting middle-range interaction parameters are given in Table 5. The addition of these binary interaction coefficients enables the use of CaBr$_2$- and MgBr$_2$-containing organic-inorganic mixture data for the fit of main group ↔ ion interactions. Figure 9 shows the calculated water activity and molal mean activity coefficients of the bromide systems in comparison with the experimental data used in the AIOMFAC fit. As

for most binary aqueous electrolyte systems, the agreement between AIOMFAC and the measurements is excellent and the extrapolation to high ionic strength (low water content/RH), where experimental data are lacking, appears to behave in a physically reasonable manner.

5 Revised implementation of $NH_4^+ \,|\, H^+ \,|\, HSO_4^- \,|\, SO_4^{2-}$ interactions

Due to an erroneous implementation of the $R_{c,c'}$ term of Eq. (4) in the previous AIOMFAC source code, the reported values of $R_{NH_4^+,H^+}$ in Zuend et al. (2008) led to larger deviations at high concentrations in the water + sulfuric acid + ammonium sulfate system. Although this does not directly affect the binary water + sulfuric acid system, we revised related interaction parameters involved in the water + sulfuric acid + ammonium bisulfate system to ensure accurate model calculations for different molar mixing ratios of $(NH_4)_2SO_4 : H_2SO_4$. The redetermined parameters are given in Tables 5 and 6. The experimental datasets used in the revision of theses parameters are listed in Table 4. The new AIOMFAC parameterization and measurements for this system with different $(NH_4)_2SO_4 : H_2SO_4$ mixing ratios (3 : 1, 2 : 1, 1 : 1, 1 : 2, and 0 : 1) are shown in Fig. 10.

5.2 Extended set of main group ↔ ion interaction parameters

The ~250 middle-range main group ↔ ion interaction parameters $b_{k,i}^{(1)}$ and $b_{k,i}^{(2)}$ (Eq. 5) have been determined by a simultaneous AIOMFAC fit to the whole database using the global optimization methods described in Appendix A1. Table 7 reports the parameters organized in the form of an interaction matrix as done in Fig. 8. While Table 7 provides the numerical values for each main group ↔ ion interaction parameter, Fig. 8 reveals the estimated degree of confidence associated with each of these interaction parameters (based merely on statistical considerations of data availability, i.e., without attempted judgment of data quality). This estimated degree of confidence is low for a substantial fraction of the interaction parameters and indicates where new

measurements would be most beneficial for a further improvement of AIOMFAC.

The extension of AIOMFAC with the new middle-range interaction parameters in conjunction with the versatility of the group-contribution concept allows the computation of activity coefficients for thousands of mixtures. Thus, here we can demonstrate only a
5   small fraction of the model's capabilities and applications. In general, the performance of a group-contribution model cannot be judged by comparison of calculations with only a few experimental datasets; rather, the model's overall performance should be evaluated based on a large ensemble of comparisons between measured and computed data. This is essentially the idea and objective of the parameter optimization proce-
10   dure. Figures showing the experimental data and corresponding AIOMFAC results of all datasets used for the determination of the interaction parameters are provided in the Supplement to this article. In the following, we will discuss measurements and AIOMFAC calculations for a selection of mixtures, representing examples for systems containing different organic functional groups.

15   ## 5.3   Examples of AIOMFAC calculations

Organic acids

Dicarboxylic acids account to a considerable fraction of the identified water-soluble organic aerosol constituents. Hence, there is a need for accurate model predictions of activity coefficients and potential phase separations for mixtures of inorganic salts
20   with dicarboxylic acids covering a wide range of relative humidities. Mixtures containing C_2 to C_6 dicarboxylic acids have been used in conjunction with the determination of the AIOMFAC parameters. Figure 11 shows a comparison of AIOMFAC calculations with different water activity measurements of the ternary system water + malonic acid + $(NH_4)_2SO_4$. The fixed molar ratio of malonic acid to ammonium sulfate of 1 : 1 in
25   the experiments enables a direct comparison with corresponding model curves. Overall, the agreement between the AIOMFAC water activity curve and the experimental data is very good. Especially at high water contents above the deliquescense RH of

(NH$_4$)$_2$SO$_4$ (a_w = 0.8), the agreement is excellent. At lower water contents, AIOMFAC predictions and EDB measurements of liquid particles (on the dehydration branch of the humidogram, i.e., supersaturated solutions) are in good agreement while the data obtained from micro-Raman measurements exhibit more scatter, but within their own variability agree with the model. The calculated curves showing the activity of malonic acid and the mean molal activity coefficient of ammonium sulfate in Fig. 11 demonstrate thermodynamically reasonable and consistent AIOMFAC behavior over a wide composition range (and beyond the range of measurements). The dotted curves, representing model sensitivities for the different quantities with respect to compositional changes on the order of x^{tol} = 0.01, show that the model sensitivity for this system is relatively low and increases only at compositions where a component is less abundant than x^{tol}.

Figure 12 shows a comparison of experimental data with AIOMFAC results for the systems water + malic acid + malonic acid + maleic acid + glutaric acid + methylsuccinic acid, saturated with the salts NaCl, panels (a) and (b), and NH$_4$NO$_3$, panels (c) and (d), respectively. These systems with five different dicarboxylic acids (M5 mixture of Marcolli et al., 2004a) demonstrate the ability of AIOMFAC to compute activities and SLE of multicomponent mixtures. Calculated water activities agree well with the experimental findings. The relative deviations between model and measurements in case of the solubility data are on the order of up to 11 %, still in good agreement with respect to an absolute mole fraction composition scale.

For these two systems, AIOMFAC slightly underpredicts the salt solubilities at moderate organic contents, which implies that the IAP reaches the solubility limit value already at lower x(salt) than found experimentally. This means that the AIOMFAC parameterization of interactions between the ions and the different organic main groups involved (CH$_n$, COOH, C=C, OH) slightly overpredicts here the effect on the IAP. For other mixtures at SLE containing the same functional groups, AIOMFAC sometimes overpredicts the solubility of the salt, so that this presents a trade-off, inherent to the parameter optimization with the group-contribution concept. If one assumes ideal mixing

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for these systems, the resulting solubility limit curve is a parallel line to the abscissa at the level of the value for x'(water) = 1.0, i.e., x(salt) = 0.1 in case of the NaCl containing system. This would clearly lead to much higher deviations (up to 125 %) between calculated and measured x(salt) values and demonstrates the necessity of incorporating non-ideal interaction effects.

Phenolic compounds

Figure 13 shows a comparison of experimental and calculated LLE and SLE data of ternary water + salt/acid systems containing phenolic compounds. In this figure, the number of functional groups substituting hydrogen atoms on the benzene ring increases from panel (a), phenol (ACH_n, $ACOH$), to (d), syringic acid (ACH_n, $ACOH$, $COOH$, $(CH_nO)_2$), accompanied by an increase in the O : C ratio of the phenolic compounds. The LLE system water + phenol + HCl at 285 K shown in panel (a) of Fig. 13 is an example of a dataset, for which the AIOMFAC based computation of the LLE phase compositions does not agree well with the measurements. A closer look reveals that the experimental data describe a liquid-liquid phase separation already for the electrolyte-free water + phenol system (at x'(HCl) = 0.0), while the phase equilibrium computation for this tie-line suggests a single liquid phase. This means that the UNIFAC description of the electrolyte-free system at this temperature is not very accurate – as AIOMFAC reduces to UNIFAC for electrolyte-free mixtures. Apparently there are larger uncertainties regarding the UNIFAC description of this system that are not caused by organic main group ↔ ion interactions. This model inaccuracy explains, at least to some extent, the deviations between AIOMFAC and measurements. While AIOMFAC essentially calculates activity coefficients for a given mixture composition, i.e., a single mixed phase, the number of coexisting phases of a thermodynamic system have to be computed with a phase equilibrium model on the basis of an activity coefficient model (here AIOMFAC). We use the phase equilibrium model of Zuend et al. (2010) to compute the number of phases and corresponding compositions to compare AIOMFAC with experimental LLE data as described in Sect. 4.3. The current version

of this phase equilibrium model limits the number of coexisting liquid phases to a maximum of two. Since for the comparisons here we a priori know the number of coexisting liquid phases from the experimental data, which is two for all considered LLE datasets, this limitation comes with no consequences. The water + phenol system of Fig. 13a shows that the phase equilibrium model still reserves the possibility of predicting only a one-phase mixture if the Gibbs energy minimization using AIOMFAC activities suggests so. Regarding complex organic-inorganic systems of many components, where potentially more than two liquid phases coexist, ideally a partitioning model should not limit the number of liquid phases to a maximum of two. The model of Zuend et al. (2010) can be extended to allow in principle a large number of coexisting phases (only limited by Gibbs' phase rule) while computing the activity coefficients of the components in each phase using AIOMFAC. Hence, while the choice and limitations of an equilibrium phase partitioning model might affect the number of predicted phases, AIOMFAC itself is not limited by any number of phases.

Calculated and measured solubility limits of the different phenolic compounds, shown in panels (b) to (d) of Fig. 13, agree relatively well (considering the scale of the y-axis). The solubility limits of such multifunctional aromatic compounds in aqueous electrolyte solutions close to room temperature are very low, as the scaling of the y-axis indicates, leading to model sensitivity (error) bars larger than the displayed composition range. While the number of datasets to constrain the main group ↔ ion interaction parameters involved in these systems is relatively low, the inequality constraints based on the functional group polarity series effectively limit the fitting capability of AIOMFAC to those datasets. Hence, slight deviations between AIOMFAC computations and the measurements in this highly dilute concentration range are accepted with the greater benefit of maintaining physically meaningful behavior to higher concentrations. The system water + salicylic acid + KNO_3 shows almost constant solubility of salicylic acid with increasing salt concentration. This is caused by the salting-in effect of KNO_3 on salicylic acid (and other organics), a known effect of nitrate ions and, to some extent, also potassium ions in highly dilute solutions.

Levoglucosan

Levoglucosan (1,6-anhydro-β-D-glucose) is one of the most abundant single species found in tropospheric aerosols (e.g., Schauer et al., 2001; Decesari et al., 2006), commonly associated with emissions from biomass burning. As an anhydrosugar, containing alkyl, hydroxyl, and ether functionalities, levoglucosan (O:C ratio = 0.833) often serves as a proxy for water-soluble organic aerosol compounds. In Fig. 14, AIOMFAC water activities of the salt-free binary system and of three ternary water + levoglucosan + electrolyte systems are compared with EDB measurements by Lienhard et al. (2011), covering a wide range of relative humidities. The three electrolytes investigated in these mixtures are ammonium sulfate ((NH_4)$_2SO_4$), ammonium nitrate (NH_4NO_3), and ammonium bisulfate (NH_4HSO_4), all important inorganic aerosol constituents. As found by Mochida and Kawamura (2004), the fully miscible binary water + levoglucosan system follows closely the behavior of an ideal solution (Fig. 14a). Deviations from ideal mixing are predicted by AIOMFAC (UNIFAC), especially prominent for the mole fraction range $0.3 < x(\text{levoglucosan}) < 0.9$. This discrepancy is, for the most part, explained by the molecular structure of levoglucosan, which has several polar groups in close proximity, leading to relatively strong intramolecular interactions, not taken into account by UNIFAC (and the UNIFAC part within AIOMFAC). Due to these deviations in the binary system, discrepancies are also expected for the electrolyte-containing mixtures. Panels (b), (c), and (d) of Fig. 14 show that AIOMFAC underpredicts the water activities of the ternary solutions as compared to the measurements, especially at lower water contents. This is related to the deviations of UNIFAC regarding the binary system. Because the organic-free aqueous electrolyte systems are very well represented by AIOMFAC, the deviations in the ternary solutions are at least partly due to the UNIFAC part. However, in case of the ternary systems, AIOMFAC predicts water activities still more accurately than simply assuming an ideal solution. The ternary system with NH_4HSO_4, panel (d), agrees very well with the EDB data and even better than expected with regard to the deviations of the salt-free system.

One reason for this result might be, that the interactions between the functional groups of levoglucosan and (especially) the ions HSO_4^- and H^+, present in this system (with explicit treatment of partial HSO_4^- dissociation), are not well enough constrained. Consequently, the related interaction parameters were somewhat overfitted to better match this dataset and erroneously compensate to a certain extent for the deviations caused by the UNIFAC part. In this case the additional constraints based on the polarity series are less restrictive, likely because most of the organic main group $\leftrightarrow HSO_4^-$ interaction parameters are estimated based on very few datasets (see Fig. 8), leaving much flexibility to these parameters. Hence, more experimental data are required to improve the representation of systems containing bisulfate ions.

5.4   Scope and limitations of a group-contribution model

The AIOMFAC model allows thermodynamically consistent calculations of the phase behavior of mixtures of organic compounds, inorganic species, and water. These calculations are thermodynamically consistent in the way that they provide a description of a mixed organic-inorganic system that is in best simultaneous agreement with all the available thermodynamic measurements and with the laws of thermodynamics.

Of course, thermodynamic consistency is a necessary but not a sufficient requirement for "correctness". Regarding the confidence in determined interaction parameters, Fig. 8 provides a first estimate based on the number of different datasets used for the determination of a certain middle-range interaction. Table 2 offers further information concerning the data types, temperature ranges, and number of data points associated with a specific interaction parameter.

Reasons for deviations between AIOMFAC and experimental data range from uncertainties regarding measurements and lack of data, to uncertainties and limitations of the AIOMFAC expressions, their parameterization, and the underlying group-contribution concept. Hence, it is likely that a fit of AIOMFAC or of a system-specific model to a highly restricted amount of data for some systems will lead to a better description of those datasets. But such restricted approaches are feasible only for specific systems

of interest and lack the generality and predictability of a group-contribution model – the main goal of AIOMFAC. A comparison and discussion on group-contribution and system-specific activity coefficient models is given in Zuend et al. (2008). For the various reasons discussed in Sects. 3.2 and 5.3 concerning conceptual and model uncertainties, it is clear that we cannot expect AIOMFAC calculations of organic-inorganic systems to attain the same high level of accuracy as AIOMFAC or other detailed thermodynamic models, such as the AIM model (Clegg et al., 1998a,b), achieve for (organic-free) aqueous electrolyte solutions. In view of this, the new parameterization of AIOMFAC is very promising and shows that computed activity coefficients and related compositions agree reasonably well with measurements for the majority of the datasets used in this study (see Supplement).

UNIFAC-based group-contribution models allow the description of thousands of organic compounds, limited only by the availability of UNIFAC parameters for different functional groups. With regard to atmospheric chemistry, limitations of UNIFAC concern the compound classes of peroxides, peroxy acids, and peroxyacyl nitrates (PANs), which are all known products of the photochemical degradation of volatile organic compounds (VOCs), and the classes of organosulfates and organonitrates, suggested to be formed in the particle phase (e.g., Chan et al., 2010; Surratt et al., 2010). Although UNIFAC parameters for a subset of these functionalities became available recently (Wittig et al., 2003; Compernolle et al., 2009), the UNIFAC parameter matrix is still incomplete because not all interactions with other common functional groups (including some of those used in AIOMFAC) have been parameterized to date. In addition to these UNIFAC (SR-part) related limitations, the full extension of AIOMFAC to these functional groups would also require experimental data of organic-inorganic systems to determine the middle-range interactions with inorganic ions.

One of the most challenging tests for a group-contribution activity coefficient model is the prediction of liquid-liquid phase equilibria compositions, since for such computations, a good representation of the activities of all system components is crucial. AIOMFAC shows this ability for many different LLE datasets considered. However,

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there are some LLE datasets that reveal larger deviations compared to AIOMFAC computations, often due to uncertainties in the UNIFAC SR-part or system-specific LLE behavior that is not captured by the interaction expressions and associated parameters determined with the objective of good overall model behavior.

AIOMFAC permits predictions of activity coefficients for mixtures that have not been part of the database for the parameter optimization, as long as all required functional groups and ions are part of the determined parameter matrix. This is a main advantage of the group-contribution concept. However, it is at present not possible to provide a quantitative estimate of how well AIOMFAC will perform for mixtures that were not part of the database used for the parameter determination. Qualitatively, one can expect the model to perform well for systems containing similar compounds as used in the parameter optimization database. Furthermore, predictions of water activities are expected to be more accurate than predicted LLE phase diagrams. The complexity of an organic compound in terms of size, number, and variety of functional groups is one of the factors influencing the accuracy of AIOMFAC and UNIFAC predictions. Since simple organic molecules composed of only a few different functional groups make up the majority of the parameterization database, the accuracy of AIOMFAC predictions can be expected to decrease with increasing structural complexity of organic compounds. Activity coefficient predictions for complex multifunctional organic compounds are less accurate, because the group-contribution concept offers only very limited means to account for intramolecular interactions between neighboring functional groups – a liquid phase is basically treated as a solution of individual functional groups (solution-of-groups concept). However, structural complexity of individual organic compounds should not be confused with number of components in a mixture. Mixtures consisting of tens to many hundreds of compounds do not need to become less accurate with increasing number of components. In fact, the solution-of-groups concept implies that AIOMFAC results are unaffected by the number of different components a set of functional groups belongs to. Therefore, AIOMFAC is well suited for computations of activity coefficients in multicomponent organic-inorganic mixtures, such as

atmospheric aerosol mixtures, expected to contain up to a few thousands of different organic compounds exhibiting a wide spectrum in terms of molecular structure and polarity.

Other factors influencing the accuracy level of AIOMFAC calculations are the salt and water contents of mixtures. The accuracy of predictions is expected to decrease with an increase of the salt content in a mixture, especially if the water content is decreased at the same time. The design and parameterization of the AIOMFAC model results in a better performance for water-rich electrolyte systems than for organic-rich electrolyte systems.

5.5 Implications for atmospheric aerosol modeling

The AIOMFAC model allows thermodynamically rigorous calculations of the phase behavior of mixtures of organic compounds, inorganic species, and water. Many organic compounds and inorganic ions, representing important species and compound classes found in atmospheric aerosol samples, have been used to determine AIOMFAC model parameters. However, even in a laboratory chamber experiment, where mass spectrometry of both gas and particle phases is carried out, the molecular speciation of all the major oxidation products of volatile organic compounds that undergo gas-particle partitioning is usually unavailable. For an atmospheric aerosol particle, its molecular composition is even less accessible than in a laboratory system. Several approaches have evolved to represent the molecular properties of organic-inorganic aerosols, especially for regional and large-scale atmospheric models. From the viewpoint of gas-particle partitioning, an essential property of the organic aerosol is the distribution of the volatilities of its components. Measurement of the volatility distribution of an organic aerosol is experimentally accessible with the thermodenuder method (e.g., Wehner et al., 2002; An et al., 2007; Faulhaber et al., 2009). Volatility can be expressed in terms of vapor pressures, gas-phase saturation mass concentrations, or enthalpies of vaporization from a liquid mixture. However, volatility alone is not sufficient to constrain organic aerosol properties. Other properties that have been proposed to represent the

organic aerosol include the O : C atomic ratio of different compounds in the aerosol mixture and the distribution of carbon numbers and/or polarity of the components. Various two-dimensional organic aerosol representations have been proposed, involving mean carbon oxidation state vs. carbon number (Kroll et al., 2011), carbon number vs. polarity (Pankow and Barsanti, 2009) and O : C ratio vs. volatility (Jimenez et al., 2009). Use of an aerosol mass spectrometer enables indirect measurement of the elemental aerosol composition and, hence, of the O : C ratio. A challenge is to relate the other properties to measurable quantities. A detailed thermodynamic model like AIOMFAC is valuable in generating predictions of gas-particle partitioning and phase behavior for well-defined molecular mixtures that approximate that of the actual aerosol; this includes the sensitivity of partitioning to RH and to addition or removal of individual classes of molecules. In this way, AIOMFAC can be used to evaluate and improve the performance of the more empirical organic aerosol models based on volatility and polarity.

AIOMFAC can also be used as a thermodynamic module to calculate phase partitioning and reaction rates in detailed aerosol and cloud-water chemistry models (e.g., Wolke et al., 2005; Deguillaume et al., 2009). Furthermore, using AIOMFAC as a benchmark model, simplified and computationally more efficient activity coefficient parameterizations of non-ideal organic-inorganic mixing can be developed, e.g., similarly as done for inorganic mixtures by Topping et al. (2009).

6 Conclusions

A new and extensive room temperature parameterization of the thermodynamic group-contribution activity coefficient model AIOMFAC is presented. Thermodynamic equilibrium data of mixed organic-inorganic systems from the literature are critically assessed and used in combination with new measurements to establish a comprehensive database for the determination of AIOMFAC model parameters. Important issues regarding deficiencies of the database, uncertainties of experimental data, and

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underlying AIOMFAC model uncertainties and sensitivities are discussed and considered. The high-dimensional global minimization problem to determine optimal interaction parameters between organic functional main groups and inorganic ions is solved with a novel combination of powerful optimization algorithms. As a result, 250 new interaction parameters are obtained, describing interactions between 11 important organic functional groups and 12 inorganic ions, allowing the calculation of activity coefficients in multicomponent organic-inorganic mixtures containing thousands of different organic compounds. With this new set of interaction parameters, AIOMFAC is arguably the most versatile activity coefficient model in that it combines a group-contribution method with an accurate electrolyte solution model. The applied methodology is shown to efficiently calculate solubility limits of salts and organics and phase compositions of LLE and VLE systems.

The new parameterization of AIOMFAC achieves generally good agreement with a large number of experimental datasets. The lack of data to constrain all activity coefficients in ternary and higher-dimensional systems is likely the most important limitation of the new AIOMFAC parameterization. Hence, some of the determined interaction parameters might be subject to adjustments in future work if new and more accurate measurements suggest a revision. There are a few datasets revealing larger deviations for complex mixtures. Various causes might be responsible for these larger deviations: uncertainties in the UNIFAC short-range part of AIOMFAC, limitations in the parameter optimization database that lead to insufficiently constrained interaction parameters, and/or highly system-specific behavior that is incompatible with the currently used expressions for the description of organic-inorganic interactions with only two middle-range parameters.

The AIOMFAC framework is open to extension to further functional groups, e.g., to describe atmospherically relevant organosulfates and organonitrates, provided that required thermodynamic data on such systems become available. Furthermore, although the current selection of functional groups and ions aims at atmospheric applications of the model, the general thermodynamic treatment is also valid for applications in other

scientific fields.

A website is in preparation to enable easy access to AIOMFAC and allow online calculations of activity coefficients of user-specified mixtures.

Appendix A

A1 Global optimization

The parameter optimization problem to solve here is to minimize a multidimensional (~250-D), multimodal, overdetermined, nonlinear, coupled, and bound-constrained objective function. Due to the high dimensionality, and nonlinear coupling of the fit parameters, this minimization problem is a genuine challenge for any global optimization method. However, in case of a parameter optimization problem it is sufficient to find a "good" local minimum, rather than the global minimum. A practical limitation exists as the many data points involved, lead to high computational costs for each objective function evaluation. In order to restrict the computation time and to limit the parameter space to a feasible domain, we ran tests with subsets of the database to find appropriate parameter bounds for the final optimization computations. Setting conservative parameter bounds also helps to confine the behavior of AIOMFAC when used for predictions beyond its tested composition range, especially in the case of interaction parameters that are constrained by a rather limited amount of experimental data points.

Efficient local minimization methods, such as Levenberg-Marquardt, or methods that minimize a function with a dimension-wise approach, such as classical Downhill-Simplex, depend on a good initial guess and fail in the present application. Rigorous deterministic global optimization methods based on derivatives of the objective function (Jacobian, Hessian matrices) scale exponentially with the number of dimensions and therefore are impractical here due to extremely high computational costs (hundreds of years of calculation time). Despite active developments in the field of numerical global optimization, many global optimization methods are suited only for problems of lower

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dimensionality. Moreover, many benchmark functions used to test and compare optimization algorithms are easy to solve compared to the problem here. After testing different global optimization algorithms with practical phase separation and parameter optimization problems, we have formulated a combination of algorithms to solve the parameter optimization problem. First, we use a modified Best-of-Random Differential Evolution (BoRDE) algorithm variant (DE/BoR/1/bin) (Lin et al., 2011) with a population size of 100 to explore the parameter space and to locate a minimum of F_{obj} subject to the polarity series constraints. Second, the global trust region method BOBYQA of Powell (2009) is applied to further refine the solution. Finally, the Downhill-Simplex algorithm by Nelder and Mead (1965) is used to fully converge to the minimum.

We modified the BoRDE algorithm to achieve self-adaptive parameter setting of the Differential Evolution parameters F and CR. To achieve this, BoRDE is combined with the competitive parameter setting strategy DEBEST by Tvrdik (2006) in the same way as described in Appendix A of Zuend et al. (2010). This Differential Evolution variant provides a good balance between exploring the parameter space (diversity) and converging to a minimum in reasonable time (computational efficiency). The reliability of finding a "good" minimum and the self-adaptive parameter setting make this BoRDE variant a robust and practical method for the minimization of high-dimensional objective functions.

A2 Own measurements

Water activity and solubility measurements have been conducted to provide some additional datasets for systems where literature data is scarce. Tables 8–20 show data of bulk water activity measurements of several ternary water + dicarboxylic acid + salt systems. An AquaLab Model 3TE (830 Decagon Devices, USA) water activity meter has been used for these measurements close to room temperature. The performance of the instrument was frequently controlled and readjusted with reference samples of pure water and 8.75 M LiCl solutions to ensure accuracy. Samples were prepared using chemicals purchased from Sigma-Aldrich with purities of ≥ 99 % mixed with distilled

deionized water (resistivity $\geq$ 15 MΩ cm) added using a 4 mL volumetric flask. When present, the compositions of the aqueous solutions were corrected for water of crystallization in salt hydrates.

Solid-liquid equilibria compositions have been measured for several aqueous electrolyte solutions saturated with (anhydrous) 2,4-dihydroxybenzaldehyde, shown in Table 21. All inorganic salts used for those solubility measurements had purities of $\geq$ 99 % except for magnesium nitrate hexahydrate which was $\geq$ 98 %. The solubility of 2,4-dihydroxybenzaldehyde in pure water was determined first, then the solubilities of the organic-inorganic mixtures. The solubilities were determined by having a fixed mass of inorganic salt dissolved in 4 ml of distilled deionized water and by subsequently adding small amounts of the organic to the solution which was then left for equilibriation at 298 K over 24 h. This procedure was repeated until the solubility limit had been reached. Based on the increments in mass added to the mixture we estimate the error to be less than 20 % (by weight).

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/11/15297/2011/ acpd-11-15297-2011-supplement.pdf.

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Table 1. Coefficients for the Gibbs-Duhem-Margules parameterization fitted to salt-free binary VLE data.

Binary system components	p (kPa) [a]	T (K) [a]	Coefficients of 4-parameter fit (–)				Exp. data
			c_1	c_2	c_3	c_4	
water(1) + formic acid(2)	101.3	375–381	-3.02194×10^{-1}	7.34748×10^{-2}	1.57832×10^{-1}	-6.52176×10^{-2}	[b]
water(1) + acetic acid(2)	98.8	373–386	6.05562×10^{-1}	1.58468×10^{-1}	1.66632×10^{-1}	1.12213×10^{-1}	[c]
water(1) + acetone(2)	101.3,80.0	323–368	1.79411	2.77094×10^{-1}	1.89513×10^{-1}	-1.14564×10^{-1}	[d]
water(1) + tetrahydrofuran(2)	101.3	336–338	2.27524	2.76082×10^{-1}	4.88769×10^{-1}	4.38607×10^{-1}	[e]
water(1) + ethyl acetate(2)	101.3	343–346	2.36413	2.31960×10^{-1}	5.23751×10^{-1}	3.72833×10^{-1}	[f]
ethyl acetate(1) + ethanol(2)	101.3	345–349	8.74984×10^{-1}	1.64586×10^{-2}	-9.86961×10^{-2}	-5.90410×10^{-2}	[g]
water(1) + 1-propanol(2)	101.3	360–371	1.63307	5.52340×10^{-1}	3.59556×10^{-1}	3.80381×10^{-1}	[h]
water(1) + 2-propanol(2)	101.3,44–82	353–372,384	1.52632	5.00563×10^{-1}	2.84293×10^{-1}	1.84488×10^{-1}	[i]
water(1) + ethanol(2)	101.3	351–372	1.20197	2.96224×10^{-1}	1.49670×10^{-1}	4.79250×10^{-2}	[j]
water(1) + ethanol(2)	12–30	307–323	1.18990	3.15496×10^{-1}	-2.48741×10^{-2}	-1.21881×10^{-1}	[k]

[a] Pressure and temperature ranges are stated with respect to the experimental data used for the fit.
Experimental data references: [b] Yun et al. (1998), [c] Narayana et al. (1985), [d] Brunjes and Bogart (1943); Al-Sahhaf and Jabbar (1993), [e] Sada et al. (1975b), [f] Rajendran et al. (1991), [g] Topphoff et al. (2001), [h] Vercher et al. (1999); Morrison et al. (1990); Gmehling et al. (1981); Lin et al. (1993), [i] Kato et al. (1971); Sada et al. (1975b); Morrison et al. (1990); Lin et al. (1993); Gmehling et al. (1981); Gironi and Lamberti (1995); Rajendran et al. (1991), [j] Gmehling et al. (1981); Kurihara et al. (1993); Johnson and Furter (1957); Kirschbaum and Gerstner (1939), [k] Kirschbaum and Gerstner (1939); Gmehling et al. (1981).

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Table 2. Components, main groups, temperature range, number of data points (N_d), initial weighting (w_d^{init}) and references of "water + organic + inorganic salt/acid" datasets used for the middle-range parameterization of organic main group ↔ ion interactions.

Organic compounds [a]	Org. main groups	Inorg. salts/acids	T (K)	Data type [b]	N_d	w_d^{init}	Reference
water + alcohol/polyol/sugar + salt /acid systems							
ethanol	CH_n, OH	$(NH_4)_2SO_4$	298	LLE	6	0.30	Wang et al. (2010)
2-propanol	CH_n, OH	$(NH_4)_2SO_4$	298	LLE	4	1.00	Sun et al. (2009)
tert-butanol	CH_n, OH	$(NH_4)_2SO_4$	298	LLE	1	1.00	Kiss and R. (2003)
glycerol	CH_n, OH	$(NH_4)_2SO_4$	298	a_w(bulk)	10	2.00	Marcolli and Krieger (2006)
1,2,4-butanetriol	CH_n, OH	$(NH_4)_2SO_4$	298	a_w(bulk)	9	2.00	Zuend et al. (2008)
1,2-butanediol	CH_n, OH	$(NH_4)_2SO_4$	298	a_w(bulk)	8	2.00	Zuend et al. (2008)
1,4-butanediol	CH_n, OH	$(NH_4)_2SO_4$	298	a_w(bulk)	12	2.00	Marcolli and Krieger (2006)
2,4-pentanediol	CH_n, OH	$(NH_4)_2SO_4$	298	a_w(bulk)	10	2.00	Zuend et al. (2008)
1,2-hexanediol	CH_n, OH	$(NH_4)_2SO_4$	298	a_w(bulk)	12	2.00	Marcolli and Krieger (2006)
2,5-hexanediol	CH_n, OH	$(NH_4)_2SO_4$	298	a_w(bulk)	8	2.00	Zuend et al. (2008)
1,7-heptanediol	CH_n, OH	$(NH_4)_2SO_4$	298	a_w(bulk)	9	2.00	Zuend et al. (2008)
glycerol	CH_n, OH	$(NH_4)_2SO_4$	298	SLE	9	1.00	Marcolli and Krieger (2006)
1,4-butanediol	CH_n, OH	$(NH_4)_2SO_4$	298	SLE	6	1.00	Marcolli and Krieger (2006)
1,2-hexanediol	CH_n, OH	$(NH_4)_2SO_4$	298	SLE	2	1.00	Marcolli and Krieger (2006)
levoglucosan	CH_n, OH, CH_nO	$(NH_4)_2SO_4$	291	a_w(EDB)	89	1.00	Lienhard et al. (2011)
1-propanol	CH_n, OH	$Ca(NO_3)_2$	362–372	VLE	15	0.05	Miro and Gonzalez (1958)
2-propanol	CH_n, OH	$Ca(NO_3)_2$	355–361	VLE	23	0.05	Miro and Gonzalez (1958)
ethanol	CH_n, OH	$Ca(NO_3)_2$	335–356	VLE	42	0.50	Polka and Gmehling (1994)
2-propanol	CH_n, OH	$Ca(NO_3)_2$	335–354	VLE	41	0.50	Polka and Gmehling (1994)
ethanol	CH_n, OH	$CaCl_2$	307–321	VLE	13	0.50	Meyer et al. (1991)
2-propanol	CH_n, OH	$CaCl_2$	354–356	VLE	12	0.50	Kato et al. (1971)
2-propanol	CH_n, OH	$CaCl_2$	356–368	VLE	42	0.50	Rajendran et al. (1991)
2-propanol	CH_n, OH	$CaCl_2$	348	VLE	18	0.50	Sada et al. (1975a)
1-propanol (water-free)	CH_n, OH	$CaCl_2$	361–372	VLE(org)	40	0.01	Fu (2005)
2-propanol (water-free)	CH_n, OH	$CaCl_2$	347–357	VLE(org)	40	0.01	Fu (2005)
1-butanol (water-free)	CH_n, OH	$CaCl_2$	374–392	VLE(org)	40	0.01	Fu (2005)
isobutanol (water-free)	CH_n, OH	$CaCl_2$	374–392	VLE(org)	30	0.01	Fu (2005)
ethanol, 3-methyl-1-butanol	CH_n, OH	$CaCl_2$	298	LLE	6	1.00	Aznar et al. (2000)
ethanol, 1-butanol	CH_n, OH	$CaCl_2$	298	LLE	6	1.00	Aznar et al. (2000)
D-mannopyranose	CH_n, OH, CH_nO	$CaCl_2$	298	$\gamma_\pm$	40	2.00	Yang et al. (2004)
D-ribofuranose	CH_n, OH, CH_nO	$CaCl_2$	298	$\gamma_\pm$	40	2.00	Yang et al. (2004)
2-propanol (water-free)	CH_n, OH	HCl	298	$\gamma_\pm$	5	2.00	Roy et al. (1972b)
1-propanol (water-free)	CH_n, OH	HCl	298	$\gamma_\pm$	7	2.00	Roy et al. (1971d)
2-propanol	CH_n, OH	HCl	298	$\gamma_\pm$	8	2.00	Roy et al. (1971a)
glycerol	CH_n, OH	HCl	298	$\gamma_\pm$	11	2.00	Roy et al. (1971b)
glycerol	CH_n, OH	HCl	298	$\gamma_\pm$	22	2.00	Knight et al. (1953)
1-butanol	CH_n, OH	HCl	298	$\gamma_\pm$	7	2.00	Roy et al. (1972a)
tert-butanol	CH_n, OH	HCl	298	$\gamma_\pm$	23	2.00	Roy et al. (1971c)
ethanol	CH_n, OH	HCl	298	$\gamma_\pm$	119	2.00	Deyhimi and Karimzadeh (2009)
2-propanol	CH_n, OH	HCl	298	$\gamma_\pm$	104	2.00	Deyhimi and Karimzadeh (2010)
ethanol	CH_n, OH	K_2SO_4	298	SLE	12	1.00	Fox and Gauge (1910)

Table 2. Continued.

Organic compounds [a]	Org. main groups	Inorg. salts/acids	T (K)	Data type [b]	N_d	w_d^{init}	Reference
1-propanol	CH_n, OH	K_2SO_4	298	SLE	16	1.00	Taboada et al. (2002)
2-propanol	CH_n, OH	K_2SO_4	303	SLE	13	1.00	Mydlarz et al. (1989)
2-propanol	CH_n, OH	K_2SO_4	293	SLE	11	0.80	Mydlarz et al. (1989)
ethanol, 1-pentanol	CH_n, OH	K_2SO_4	298	LLE	10	1.00	Aznar et al. (2000)
1-butanol	CH_n, OH	KBr	298	LLE	10	1.00	Li et al. (1995)
1-propanol	CH_n, OH	KBr	359–362	VLE	30	0.05	Morrison et al. (1990)
ethanol	CH_n, OH	KBr	354–357	VLE	36	0.50	Burns and Furter (1975)
ethanol	CH_n, OH	KBr	303	SLE	11	0.10	Taylor (1897)
1-butanol	CH_n, OH	KBr	298	LLE	11	1.00	Al-Sahhaf and Kapetanovic (1997)
tert-butanol, 1-butanol	CH_n, OH	KBr	293	LLE	14	1.00	Pereira and Aznar (2006)
tert-butanol, 1-butanol	CH_n, OH	KBr	313	LLE	5	1.00	Pereira and Aznar (2006)
ethanol, 1-pentanol	CH_n, OH	KBr	298	LLE	20	1.00	Aznar et al. (2000)
ethanol	CH_n, OH	KCl	350–369	VLE	11	0.50	Johnson and Furter (1965)
1-propanol	CH_n, OH	KCl	361–372	VLE	8	0.50	Johnson and Furter (1965)
1-propanol	CH_n, OH	KCl	360–363	VLE	32	0.50	Lin et al. (1993)
1-butanol	CH_n, OH	KCl	298	LLE	8	1.00	Li et al. (1995)
1-propanol	CH_n, OH	KCl	298	LLE	9	1.00	Chou et al. (1998)
1-propanol	CH_n, OH	KCl	298	LLE	4	1.00	Gomis et al. (1996)
1-butanol	CH_n, OH	KCl	298	LLE	9	1.00	Gomis et al. (1996)
2-butanol	CH_n, OH	KCl	298	LLE	9	1.00	Gomis et al. (1996)
isobutanol	CH_n, OH	KCl	298	LLE	9	1.00	Gomis et al. (1996)
ethanol	CH_n, OH	KCl	298	$\gamma_\pm$	60	2.00	Lopes et al. (1999)
ethanol, 1-pentanol	CH_n, OH	KCl	298	LLE	19	1.00	Aznar et al. (2000)
1,2-ethanediol	CH_n, OH	KCl	298	$\gamma_\pm$	96	2.00	Ma et al. (2010)
ethanol	CH_n, OH	KNO_3	351–369	VLE	8	0.50	Rieder and Thompson (1950)
ethanol	CH_n, OH	KNO_3	351–364	VLE	49	0.50	Vercher et al. (1996)
ethanol	CH_n, OH	KNO_3	303	SLE	10	1.00	Bathrick (1896)
1-propanol	CH_n, OH	Li_2SO_4	298	LLE	5	1.00	Taboada (2003)
ethanol	CH_n, OH	LiBr	333	VLE	19	0.05	Rudakoff et al. (1972)
2-propanol	CH_n, OH	LiBr	348	VLE	18	0.50	Sada et al. (1975a)
2-propanol	CH_n, OH	LiBr	353–357	VLE	28	0.50	Lin et al. (1993)
ethanol	CH_n, OH	LiCl	298	$\gamma_\pm$	42	2.00	Hu et al. (2008)
ethanol	CH_n, OH	LiCl	298	$\gamma_\pm$	64	2.00	Hernandez-Luis et al. (2008)
2-propanol	CH_n, OH	LiCl	348	VLE	26	0.50	Sada et al. (1975a)
2-propanol	CH_n, OH	LiCl	353–357	VLE	28	0.50	Lin et al. (1993)
1-butanol	CH_n, OH	LiCl	298	LLE	17	0.10	Al-Sahhaf and Kapetanovic (1997)
tert-butanol	CH_n, OH	LiCl	298	LLE	10	0.10	Gomis et al. (2008)
1-pentanol	CH_n, OH	LiCl	298	LLE	9	0.10	Gomis et al. (2004)
2-pentanol	CH_n, OH	LiCl	298	LLE	9	0.10	Gomis et al. (2004)
3-pentanol	CH_n, OH	LiCl	298	LLE	9	0.10	Gomis et al. (2004)
2-methyl-1-butanol	CH_n, OH	LiCl	298	LLE	9	0.10	Gomis et al. (2004)
2-methyl-2-butanol	CH_n, OH	LiCl	298	LLE	9	0.10	Gomis et al. (2004)
ethanol, (water-free)	CH_n, OH	$LiNO_3$	298	VLE(org)	10	0.50	Verevkin et al. (2006)
1-propanol, (water-free)	CH_n, OH	$LiNO_3$	370–374	VLE(org)	17	0.50	Vercher et al. (2002)
1-propanol	CH_n, OH	$LiNO_3$	361–374	VLE	103	0.50	Vercher et al. (2002)

Table 2. Continued.

Organic compounds [a]	Org. main groups	Inorg. salts/acids	T (K)	Data type [b]	N_d	w_d^{init}	Reference
2-propanol	CH_n, OH	$MgBr_2$	353–359	VLE	33	0.50	Gironi and Lamberti (1995)
1,3-nonanediol	CH_n, OH	$MgCl_2$	298	LLE	1	1.00	Putnin' et al. (1974)
2-propanol	CH_n, OH	$MgCl_2$	313	SLE	5	0.50	Balaban and Kuranov (1999)
2-propanol	CH_n, OH	$MgCl_2$	313	SLE	9	0.01	Balaban and Kuranov (1999)
2-propanol	CH_n, OH	$MgCl_2$	313	SLE	7	0.01	Balaban and Kuranov (1999)
2-propanol	CH_n, OH	$MgCl_2$	353–370	VLE	72	0.50	Gironi and Lamberti (1995)
tert-butanol, 1-butanol	CH_n, OH	$MgCl_2$	293	LLE	14	1.00	Pereira and Aznar (2006)
tert-butanol, 1-butanol	CH_n, OH	$MgCl_2$	313	LLE	14	0.80	Pereira and Aznar (2006)
2-propanol	CH_n, OH	$MgCl_2$, $CaCl_2$	313	VLE	38	0.50	Balaban and Kuranov (2002)
ethanol	CH_n, OH	$MgSO_4$	298	SLE	11	0.50	Zafarani-Moattar and Salabat (1997)
1-propanol	CH_n, OH	$MgSO_4$	298	LLE	6	1.00	Zafarani-Moattar and Salabat (1997)
2-propanol	CH_n, OH	$MgSO_4$	298	LLE	5	0.50	Zafarani-Moattar and Salabat (1997)
tert-butanol	CH_n, OH	$MgSO_4$	298	LLE	6	1.00	Zafarani-Moattar and Salabat (1997)
ethanol	CH_n, OH	Na_2SO_4	298	LLE	3	1.00	Greve and Kula (1991)
1,2-ethanediol	CH_n, OH	Na_2SO_4	308	SLE	13	0.80	Vener and Thompson (1949)
1-propanol	CH_n, OH	Na_2SO_4	293	SLE	5	1.00	Brenner et al. (1992)
2-propanol	CH_n, OH	Na_2SO_4	293	SLE	10	1.00	Brenner et al. (1992)
tert-butanol	CH_n, OH	Na_2SO_4	293	SLE	5	1.00	Brenner et al. (1992)
1-propanol	CH_n, OH	Na_2SO_4	297–353	LLE	12	1.00	Brenner et al. (1992)
2-propanol	CH_n, OH	Na_2SO_4	302–353	LLE	8	1.00	Brenner et al. (1992)
2-propanol	CH_n, OH	Na_2SO_4	308	LLE	8	1.00	Lynn et al. (1996)
tert-butanol	CH_n, OH	Na_2SO_4	308	LLE	12	1.00	Lynn et al. (1996)
tert-butanol	CH_n, OH	Na_2SO_4	296–353	LLE	13	0.10	Brenner et al. (1992)
2-propanol	CH_n, OH	Na_2SO_4	298	SLE	11	1.00	Brenner et al. (1992)
ethanol	CH_n, OH	Na_2SO_4	313	VLE(org)	6	0.10	Falabella et al. (2006)
1-propanol	CH_n, OH	Na_2SO_4	313	VLE(org)	5	0.10	Falabella et al. (2006)
1-butanol	CH_n, OH	Na_2SO_4	313	VLE(org)	6	0.10	Falabella et al. (2006)
1-pentanol	CH_n, OH	Na_2SO_4	313	VLE(org)	6	0.10	Falabella et al. (2006)
1-hexanol	CH_n, OH	Na_2SO_4	313	VLE(org)	6	0.10	Falabella et al. (2006)
1-propanol	CH_n, OH	NaBr	360–364	VLE	26	0.50	Morrison et al. (1990)
2-propanol	CH_n, OH	NaBr	353–358	VLE	55	0.50	Morrison et al. (1990)
1-propanol	CH_n, OH	NaBr	298	LLE	11	0.50	Chou et al. (1998)
1-butanol	CH_n, OH	NaBr	298	LLE	18	1.00	Al-Sahhaf and Kapetanovic (1997)
D-mannopyranose	CH_n, OH, CH_nO	NaBr	298	$\gamma_\pm$	32	2.00	Yang et al. (2004)
D-ribofuranose	CH_n, OH, CH_nO	NaBr	298	$\gamma_\pm$	32	2.00	Yang et al. (2004)
ethanol	CH_n, OH	NaCl	298	$\gamma_\pm$	28	2.00	Esteso et al. (1989)
ethanol	CH_n, OH	NaCl	298	$\gamma_\pm$	25	2.00	Esteso et al. (1989)
ethanol	CH_n, OH	NaCl	298	$\gamma_\pm$	24	2.00	Esteso et al. (1989)
ethanol	CH_n, OH	NaCl	298	$\gamma_\pm$	17	1.00	Esteso et al. (1989)
ethanol	CH_n, OH	NaCl	298	$\gamma_\pm$	15	0.50	Esteso et al. (1989)
ethanol	CH_n, OH	NaCl	298	$\gamma_\pm$	14	0.50	Esteso et al. (1989)
ethanol	CH_n, OH	NaCl	298	SLE	7	1.00	Pinho and Macedo (1996)
ethanol	CH_n, OH	NaCl	306–313	VLE	16	0.50	Meyer et al. (1991)
ethanol	CH_n, OH	NaCl	350–361	VLE	13	0.50	Johnson and Furter (1965)
ethanol	CH_n, OH	NaCl	316–332	VLE	14	0.50	Meyer et al. (1991)

Table 2. Continued.

Organic compounds [a]	Org. main groups	Inorg. salts/acids	T (K)	Data type [b]	N_d	w_d^{init}	Reference
1-propanol	CH_n, OH	NaCl	359–363	VLE	36	0.50	Morrison et al. (1990)
1-propanol	CH_n, OH	NaCl	362–375	VLE	10	0.50	Johnson and Furter (1965)
1-propanol	CH_n, OH	NaCl	360–365	VLE	27	0.50	Lin et al. (1993)
2-propanol	CH_n, OH	NaCl	353–362	VLE	56	0.00	Rajendran et al. (1991)
glycerol	CH_n, OH	NaCl	298	a_w(bulk)	10	2.00	Marcolli and Krieger (2006)
1,4-butanediol	CH_n, OH	NaCl	298	a_w(bulk)	10	2.00	Marcolli and Krieger (2006)
ethanol	CH_n, OH	NaCl	298	$\gamma_\pm$	48	2.00	Lopes et al. (2001)
1-propanol	CH_n, OH	NaCl	298	LLE	11	1.00	De Santis et al. (1976)
2-propanol	CH_n, OH	NaCl	298	LLE	8	1.00	De Santis et al. (1976)
1-butanol	CH_n, OH	NaCl	298	LLE	20	1.00	De Santis et al. (1976)
isobutanol	CH_n, OH	NaCl	298	LLE	20	1.00	De Santis et al. (1976)
2-butanol	CH_n, OH	NaCl	298	LLE	20	1.00	De Santis et al. (1976)
tert-butanol	CH_n, OH	NaCl	298	LLE	14	1.00	De Santis et al. (1976)
1-propanol	CH_n, OH	NaCl	298	LLE	8	1.00	Chou et al. (1998)
1-propanol	CH_n, OH	NaCl	298	LLE	5	1.00	Gomis et al. (1994)
2-propanol	CH_n, OH	NaCl	298	LLE	5	1.00	Gomis et al. (1994)
1-butanol	CH_n, OH	NaCl	298	LLE	10	1.00	Li et al. (1995)
2-butanol	CH_n, OH	NaCl	298	LLE	9	1.00	Gomis et al. (1996)
isobutanol	CH_n, OH	NaCl	298	LLE	9	1.00	Gomis et al. (1996)
tert-butanol	CH_n, OH	NaCl	298	LLE	8	1.00	Gomis et al. (1996)
1-butanol	CH_n, OH	NaCl	313	LLE	19	0.50	De Santis et al. (1976)
1,2-hexanediol	CH_n, OH	NaCl	298	a_w(bulk)	17	2.00	Marcolli and Krieger (2006)
glycerol	CH_n, OH	NaCl	298	SLE	9	1.00	Marcolli and Krieger (2006)
1,4-butanediol	CH_n, OH	NaCl	298	SLE	9	1.00	Marcolli and Krieger (2006)
1,2-hexanediol	CH_n, OH	NaCl	298	SLE	8	1.00	Marcolli and Krieger (2006)
1,4-dihydroxy-2-butene	CH_n, OH, C=C	NaCl	298	SLE	6	1.00	Raridon and Kraus (1971)
ethanol, 3-methyl-1-butanol	CH_n, OH	NaCl	298	LLE	9	1.00	Aznar et al. (2000)
ethanol, 1-butanol	CH_n, OH	NaCl	298	LLE	9	1.00	Aznar et al. (2000)
D-fructopyranose	CH_n, OH, CH_nO	NaCl	298	$\gamma_\pm$	56	2.00	Hernandez-Luis et al. (2004)
D-mannopyranose	CH_n, OH, CH_nO	NaCl	298	$\gamma_\pm$	32	2.00	Yang et al. (2004)
D-ribofuranose	CH_n, OH, CH_nO	NaCl	298	$\gamma_\pm$	32	2.00	Yang et al. (2004)
ethanol	CH_n, OH	NaCl, KCl	298	$\gamma_\pm$	31	2.00	Farelo et al. (2002)
ethanol	CH_n, OH	$NaNO_3$	351–373	VLE	122	0.50	Pena et al. (1996)
ethanol	CH_n, OH	$NaNO_3$	303	SLE	10	0.50	Taylor (1897)
ethanol	CH_n, OH	NH_4Br	355–358	VLE	39	0.50	Burns and Furter (1975)
ethanol	CH_n, OH	NH_4Cl	298	$\gamma_\pm$	18	2.00	Deyhimi et al. (2005)
ethanol	CH_n, OH	NH_4Cl	298	$\gamma_\pm$	18	2.00	Deyhimi et al. (2005)
ethanol	CH_n, OH	NH_4Cl	298	$\gamma_\pm$	18	2.00	Deyhimi et al. (2005)
ethanol	CH_n, OH	NH_4Cl	298	$\gamma_\pm$	18	2.00	Deyhimi et al. (2005)
ethanol	CH_n, OH	NH_4Cl	298	$\gamma_\pm$	18	2.00	Deyhimi et al. (2005)
ethanol	CH_n, OH	NH_4Cl	303	SLE	10	1.00	Bathrick (1896)
ethanol	CH_n, OH	NH_4Cl	350–366	VLE	32	0.50	Johnson and Furter (1965)
1-propanol	CH_n, OH	NH_4Cl	362–383	VLE	9	0.50	Johnson and Furter (1965)
2-propanol	CH_n, OH	NH_4Cl	298	$\gamma_\pm$	46	2.00	Deyhimi and Ghalami-Choobar (2006)
levoglucosan	CH_n, OH, CH_nO	NH_4HSO_4	291	a_w(EDB)	69	1.00	Lienhard et al. (2011)
glycerol	CH_n, OH	NH_4NO_3	298	a_w(bulk)	9	2.00	Marcolli and Krieger (2006)
1,4-butanediol	CH_n, OH	NH_4NO_3	298	a_w(bulk)	12	2.00	Marcolli and Krieger (2006)

Table 2. Continued.

Organic compounds [a]	Org. main groups	Inorg. salts/acids	T (K)	Data type [b]	N_d	w_d^{init}	Reference
1,2-hexanediol	CH_n, OH	NH_4NO_3	298	a_w(bulk)	16	2.00	Marcolli and Krieger (2006)
glycerol	CH_n, OH	NH_4NO_3	298	SLE	8	1.00	Marcolli and Krieger (2006)
1,4-butanediol	CH_n, OH	NH_4NO_3	298	SLE	11	1.00	Marcolli and Krieger (2006)
1,2-hexanediol	CH_n, OH	NH_4NO_3	298	SLE	8	1.00	Marcolli and Krieger (2006)
levoglucosan	CH_n, OH, CH_nO	NH_4NO_3	291	a_w(EDB)	73	1.00	Lienhard et al. (2011)
water + carboxylic acid + salt/acid systems							
malonic acid	CH_n, COOH	$(NH_4)_2SO_4$	298	a_w(EDB)	18	1.00	Ling and Chan (2008)
glutaric acid	CH_n, COOH	$(NH_4)_2SO_4$	298	a_w(EDB)	21	1.00	Ling and Chan (2008)
succinic acid	CH_n, COOH	$(NH_4)_2SO_4$	298	a_w(EDB)	17	1.00	Ling and Chan (2008)
succinic acid	CH_n, COOH	$(NH_4)_2SO_4$	295	a_w(bulk)	5	2.00	Choi and Chan (2002)
malonic acid	CH_n, COOH	$(NH_4)_2SO_4$	295	a_w(bulk)	5	2.00	Choi and Chan (2002)
glutaric acid	CH_n, COOH	$(NH_4)_2SO_4$	295	a_w(bulk)	10	2.00	Choi and Chan (2002)
citric acid	CH_n, COOH, OH	$(NH_4)_2SO_4$	295	a_w(bulk)	8	2.00	Choi and Chan (2002)
citric acid	CH_n, COOH, OH	$(NH_4)_2SO_4$	295	a_w(SEDB)	54	0.10	Choi and Chan (2002)
malonic acid	CH_n, COOH	$(NH_4)_2SO_4$	298	a_w(bulk)	52	2.00	Salcedo (2006)
malonic acid	CH_n, COOH	$(NH_4)_2SO_4$	298	SLE	4	1.00	Salcedo (2006)
malonic acid	CH_n, COOH	$(NH_4)_2SO_4$	298	SLE	6	1.00	Salcedo (2006)
malonic acid	CH_n, COOH	$(NH_4)_2SO_4$	297	a_w(micro-Raman)	61	0.20	Yeung and Chan (2010)
glutaric acid	CH_n, COOH	$(NH_4)_2SO_4$	297	a_w(micro-Raman)	71	0.20	Yeung and Chan (2010)
malonic acid	CH_n, COOH	$(NH_4)_2SO_4$	298	a_w(bulk)	1	2.00	Wise et al. (2003)
glutaric acid	CH_n, COOH	$(NH_4)_2SO_4$	298	a_w(bulk)	1	2.00	Wise et al. (2003)
succinic acid	CH_n, COOH	$(NH_4)_2SO_4$	298	a_w(bulk)	1	2.00	Wise et al. (2003)
oxalic acid	CH_n, COOH	$(NH_4)_2SO_4$	298	a_w(bulk)	1	2.00	Wise et al. (2003)
maleic acid	C=C, COOH	$(NH_4)_2SO_4$	298	a_w(bulk)	1	2.00	Wise et al. (2003)
malic acid	CH_n, COOH, OH	$(NH_4)_2SO_4$	298	a_w(bulk)	1	1.00	Wise et al. (2003)
M5: malic acid, malonic acid, maleic acid, glutaric acid, methylsuccinic acid	CH_n, COOH, OH, C=C	$(NH_4)_2SO_4$	298	a_w(bulk)	25	2.00	Marcolli et al. (2004a)
M5: malic acid, malonic acid, maleic acid, glutaric acid, methylsuccinic acid	CH_n, COOH, OH, C=C	$(NH_4)_2SO_4$	298	SLE	8	1.00	Marcolli et al. (2004a)
oxalic acid	CH_n, COOH	$(NH_4)_2SO_4$	293	a_w(bulk)	7	2.00	this study
malonic acid	CH_n, COOH	$(NH_4)_2SO_4$	293	a_w(bulk)	16	2.00	this study
glutaric acid	CH_n, COOH	$(NH_4)_2SO_4$	293	a_w(bulk)	9	2.00	this study
succinic acid	CH_n, COOH	$(NH_4)_2SO_4$	293	a_w(bulk)	9	2.00	this study
adipic acid	CH_n, COOH	$(NH_4)_2SO_4$	293	a_w(bulk)	3	2.00	this study
glutaric acid	CH_n, COOH	$(NH_4)_2SO_4$	291	a_w(EDB)	38	1.00	Zardini et al. (2008)
citric acid	CH_n, COOH, OH	$(NH_4)_2SO_4$	291	a_w(EDB)	62	1.00	Zardini et al. (2008)
citric acid	CH_n, COOH, OH	$(NH_4)_2SO_4$	291	a_w(EDB)	57	1.00	Zardini et al. (2008)
citric acid	CH_n, COOH, OH	$(NH_4)_2SO_4$	291	a_w(EDB)	45	1.00	Zardini et al. (2008)
2-methylglutaric acid, 3-methylglutaric acid, 2,2-dimethylsuccinic acid	CH_n, COOH	$(NH_4)_2SO_4$	291	a_w(EDB)	88	1.00	this study
maleic acid	C=C, COOH	$Ca(NO_3)_2$	293	a_w(bulk)	13	2.00	this study
propanoic acid, 1-butanol	CH_n, COOH, OH	$CaCl_2$	303	LLE	26	1.00	Zurita et al. (1998)
propanoic acid	CH_n, COOH	$CaCl_2$	333	VLE(x-y-T)	5	0.50	Banat et al. (2002)
propanoic acid	CH_n, COOH	$CaCl_2$	333	VLE(x-y-T)	20	0.50	Banat et al. (2003a)
propanoic acid	CH_n, COOH	$CaCl_2$	313	VLE(x-y-T)	5	0.50	Banat et al. (2003b)
propanoic acid	CH_n, COOH	$CaCl_2$	323	VLE(x-y-T)	15	0.50	Banat et al. (2003b)
acetic acid	CH_n, COOH	K_2SO_4	373–375	VLE	26	0.50	Narayana et al. (1985)
propanoic acid	CH_n, COOH	KBr	333	VLE(x-y-T)	5	0.50	Banat et al. (2003a)
acetic acid	CH_n, COOH	KCl	374–386	VLE	21	0.50	Narayana et al. (1985)
acetic acid	CH_n, COOH	KCl	303	SLE	9	0.50	Narayana et al. (1985)
propanoic acid	CH_n, COOH	KCl	333	VLE(x-y-T)	5	0.50	Banat et al. (2003a)
acetic acid, 1-butanol	CH_n, COOH, OH	KCl	298	LLE	38	1.00	Tan and Aravinth (1999)
propanoic acid	CH_n, COOH	KNO_3	333	VLE(x-y-T)	5	0.50	Banat et al. (2003a)
acetic acid	CH_n, COOH	KNO_3	298	SLE	1	0.01	Davidson and Geer (1933)
2-methylpropanoic acid	CH_n, COOH	LiCl	303	LLE	4	1.00	Sergeeva and Matyushinskaya (1969)

Table 2. Continued.

Organic compounds [a]	Org. main groups	Inorg. salts/acids	T (K)	Data type [b]	N_d	w_d^{init}	Reference
malonic acid	CH$_n$, COOH	LiNO$_3$	303	a_w(bulk)	12	2.00	this study
malonic acid	CH$_n$, COOH	LiNO$_3$	293	a_w(bulk)	12	2.00	this study
maleic acid	C=C, COOH	Mg(NO$_3$)$_2$	293	a_w(bulk)	7	2.00	this study
formic acid	COOH	MgCl$_2$	377–400	VLE	40	0.50	Yun et al. (1998)
citric acid	CH$_n$, COOH, OH	Na$_2$SO$_4$	298	a_w(bulk)	33	2.00	Schunk and Maurer (2004)
acetic acid	CH$_n$, COOH	Na$_2$SO$_4$	374–388	VLE	23	0.50	Narayana et al. (1985)
malonic acid	CH$_n$, COOH	Na$_2$SO$_4$	303	a_w(bulk)	8	2.00	this study
malonic acid	CH$_n$, COOH	Na$_2$SO$_4$	293	a_w(bulk)	8	2.00	this study
glutaric acid	CH$_n$, COOH	NaCl	295	a_w(SEDB)	19	1.00	Choi and Chan (2002)
malonic acid	CH$_n$, COOH	NaCl	295	a_w(bulk)	6	2.00	Choi and Chan (2002)
malonic acid	CH$_n$, COOH	NaCl	295	a_w(SEDB)	38	1.00	Choi and Chan (2002)
succinic acid	CH$_n$, COOH	NaCl	295	a_w(bulk)	6	2.00	Choi and Chan (2002)
succinic acid	CH$_n$, COOH	NaCl	295	a_w(SEDB)	22	1.00	Choi and Chan (2002)
citric acid	CH$_n$, COOH, OH	NaCl	295	a_w(bulk)	7	2.00	Choi and Chan (2002)
citric acid	CH$_n$, COOH, OH	NaCl	295	a_w(SEDB)	37	1.00	Choi and Chan (2002)
M5: malic acid, malonic acid, maleic acid, glutaric acid, methylsuccinic acid	CH$_n$, COOH, OH, C=C	NaCl	298	a_w(bulk)	10	2.00	Marcolli et al. (2004a)
M5: malic acid, malonic acid, maleic acid, glutaric acid, methylsuccinic acid	CH$_n$, COOH, OH, C=C	NaCl	298	SLE	10	1.00	Marcolli et al. (2004a)
citric acid	CH$_n$, COOH, OH	NaCl	298	a_w(bulk)	37	2.00	Schunk and Maurer (2004)
citric acid, 2-butanol	CH$_n$, COOH, OH	NaCl	298	LLE	15	1.00	Lintomen et al. (2000)
propanoic acid, 1-butanol	CH$_n$, COOH, OH	NaCl	303	LLE	19	1.00	Solimo et al. (1997)
propanoic acid	CH$_n$, COOH	NaCl	333	VLE(x-y-T)	23	0.50	Banat et al. (2002)
propanoic acid	CH$_n$, COOH	NaCl	313	VLE(x-y-T)	5	0.50	Banat et al. (2003b)
propanoic acid	CH$_n$, COOH	NaCl	323	VLE(x-y-T)	15	0.50	Banat et al. (2003b)
malonic acid	CH$_n$, COOH	NaCl	303	a_w(bulk)	8	2.00	this study
malonic acid	CH$_n$, COOH	NaCl	293	a_w(bulk)	8	2.00	this study
glutaric acid	CH$_n$, COOH	NaCl	295	a_w(EDB)	42	1.00	Pope et al. (2010)
malonic acid	CH$_n$, COOH	NaCl	295	a_w(EDB)	29	1.00	Pope et al. (2010)
acetic acid, 1-butanol	CH$_n$, COOH, OH	NaCl	298	LLE	41	1.00	Tan and Aravinth (1999)
citric acid	CH$_n$, COOH, OH	NaNO$_3$	298	a_w(bulk)	35	2.00	Schunk and Maurer (2004)
acetic acid	CH$_n$, COOH	NaNO$_3$	298	SLE	1	0.01	Davidson and Geer (1933)
malonic acid	CH$_n$, COOH	NH$_4$Br	303	a_w(bulk)	9	2.00	this study
malonic acid	CH$_n$, COOH	NH$_4$Br	293	a_w(bulk)	9	2.00	this study
maleic acid	C=C, COOH	NH$_4$Br	293	a_w(bulk)	7	2.00	this study
propanoic acid	CH$_n$, COOH	NH$_4$Cl	333	VLE(x-y-T)	5	0.50	Banat et al. (2002)
propanoic acid	CH$_n$, COOH	NH$_4$Cl	313	VLE(x-y-T)	5	0.50	Banat et al. (2003b)
propanoic acid	CH$_n$, COOH	NH$_4$Cl	323	VLE(x-y-T)	5	0.50	Banat et al. (2003b)
methacrylic acid	CH$_n$, C=C COOH	NH$_4$HSO$_4$	298	LLE	4	0.01	Obmelyukhina et al. (1979)
malonic acid	CH$_n$, COOH	NH$_4$HSO$_4$	298	a_w(bulk)	66	2.00	Salcedo (2006)
malonic acid	CH$_n$, COOH	NH$_4$HSO$_4$	298	SLE	8	1.00	Salcedo (2006)
malonic acid	CH$_n$, COOH	NH$_4$HSO$_4$	289	SLE	5	1.00	Salcedo (2006)
M5: malic acid, malonic acid, maleic acid, glutaric acid, methylsuccinic acid	CH$_n$, COOH, OH, C=C	NH$_4$NO$_3$	298	a_w(bulk)	6	2.00	Marcolli et al. (2004a)
M5: malic acid, malonic acid, maleic acid, glutaric acid, methylsuccinic acid	CH$_n$, COOH, OH, C=C	NH$_4$NO$_3$	298	SLE	6	1.00	Marcolli et al. (2004a)
malonic acid	CH$_n$, COOH	NH$_4$NO$_3$	293	a_w(bulk)	16	2.00	this study
malonic acid	CH$_n$, COOH	NH$_4$NO$_3$	303	a_w(bulk)	16	2.00	this study
acetic acid	CH$_n$, COOH	NH$_4$NO$_3$	298	SLE	1	0.01	Davidson and Geer (1933)
water + ketone + salt/acid systems							
4-methyl-2-pentanone, propanoic acid	CH$_n$, COOH, CH$_n$CO	(NH$_4$)$_2$SO$_4$	308	LLE	17	1.00	Govindarajan and Sabarathinam (1997)
4-methyl-2-pentanone, butanoic acid	CH$_n$, COOH, CH$_n$CO	(NH$_4$)$_2$SO$_4$	308	LLE	8	1.00	Govindarajan and Sabarathinam (1997)
4-methyl-2-pentanone, acetic acid	CH$_n$, COOH, CH$_n$CO	(NH$_4$)$_2$SO$_4$	308	LLE	26	1.00	Govindarajan and Sabarathinam (1995)

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Table 2. Continued.

Organic compounds [a]	Org. main groups	Inorg. salts/acids	T (K)	Data type [b]	N_d	w_d^{init}	Reference
acetone	CH_n, CH_nCO	$CaCl_2$	296	LLE	16	1.00	Bourayou and Meniai (2007)
acetone	CH_n, CH_nCO	$CaCl_2$	296	LLE	23	1.00	Bourayou and Meniai (2007)
3-methyl-2-butanone	CH_n, CH_nCO	HCl	298	LLE	3	0.05	Pilloton (1958)
4-methyl-2-pentanone	CH_n, CH_nCO	HCl	298	LLE	8	0.05	Pilloton (1958)
3-heptanone	CH_n, CH_nCO	HCl	298	LLE	3	0.05	Pilloton (1958)
2-heptanone	CH_n, CH_nCO	HCl	298	LLE	8	0.05	Pilloton (1958)
2-butanone	CH_n, CH_nCO	KBr	298	LLE	10	1.00	Li et al. (1995)
acetone	CH_n, CH_nCO	KBr	326–362	VLE	27	0.50	Al-Sahhaf and Jabbar (1993)
4-methyl-2-pentanone, propanoic acid	CH_n, COOH, CH_nCO	KCl	298	LLE	10	1.00	Roy et al. (2007)
3-methyl-2-butanone, propanoic acid	CH_n, COOH, CH_nCO	KCl	298	LLE	10	1.00	Roy et al. (2007)
2-butanone	CH_n, CH_nCO	KCl	298	LLE	8	1.00	Tan and Kannangara (2001)
2-butanone, 1-propanol	CH_n, CH_nCO, OH	KCl	298	LLE	25	1.00	Tan and Kannangara (2001)
2-butanone	CH_n, CH_nCO	KCl	298	LLE	10	1.00	Li et al. (1995)
acetone	CH_n, CH_nCO	KCl	293	SLE	5	0.80	Li et al. (2007)
acetone	CH_n, CH_nCO	KNO_3	313	SLE	9	0.60	Bathrick (1896)
2-butanone	CH_n, CH_nCO	LiCl	298	LLE	11	1.00	Al-Sahhaf et al. (1999)
acetone	CH_n, CH_nCO	LiCl	329–356	VLE	46	0.50	Al-Sahhaf and Jabbar (1993)
acetone	CH_n, CH_nCO	$MgCl_2$	293	SLE	10	0.80	Li et al. (2007)
acetone	CH_n, CH_nCO	$MgCl_2$	303	SLE	10	0.80	Li et al. (2007)
4-methyl-2-pentanone, propanoic acid	CH_n, COOH, CH_nCO	Na_2SO_4	308	LLE	20	1.00	Govindarajan and Sabarathinam (1997)
4-methyl-2-pentanone, butanoic acid	CH_n, COOH, CH_nCO	Na_2SO_4	308	LLE	11	1.00	Govindarajan and Sabarathinam (1997)
4-methyl-2-pentanone, acetic acid	CH_n, COOH, CH_nCO	Na_2SO_4	308	LLE	25	1.00	Govindarajan and Sabarathinam (1995)
4-methyl-2-pentanone	CH_n, CH_nCO	Na_2SO_4	298	LLE	4	1.00	Schunk et al. (2004)
acetone	CH_n, CH_nCO	Na_2SO_4	303–323	LLE	8	0.80	Lynn et al. (1996)
acetone	CH_n, CH_nCO	Na_2SO_4	308	LLE	6	0.80	Lynn et al. (1996)
acetone	CH_n, CH_nCO	Na_2SO_4	323	VLE(org)	5	0.10	Chai et al. (2005)
2-butanone	CH_n, CH_nCO	Na_2SO_4	323	VLE(org)	5	0.10	Chai et al. (2005)
2-pentanone	CH_n, CH_nCO	Na_2SO_4	323	VLE(org)	5	0.10	Chai et al. (2005)
2-hexanone	CH_n, CH_nCO	Na_2SO_4	323	VLE(org)	5	0.10	Chai et al. (2005)
2-heptanone	CH_n, CH_nCO	Na_2SO_4	323	VLE(org)	5	0.10	Chai et al. (2005)
2-butanone	CH_n, CH_nCO	NaBr	298	LLE	11	1.00	Al-Sahhaf et al. (1999)
acetone	CH_n, CH_nCO	NaBr	324–352	VLE	47	0.50	Al-Sahhaf and Jabbar (1993)
4-methyl-2-pentanone, propanoic acid	CH_n, COOH, CH_nCO	NaCl	308	LLE	26	1.00	Govindarajan and Sabarathinam (1997)
4-methyl-2-pentanone, butanoic acid	CH_n, COOH, CH_nCO	NaCl	308	LLE	6	1.00	Govindarajan and Sabarathinam (1997)
4-methyl-2-pentanone, acetic acid	CH_n, COOH, CH_nCO	NaCl	308	LLE	28	1.00	Govindarajan and Sabarathinam (1995)
4-methyl-2-pentanone, propanoic acid	CH_n, COOH, CH_nCO	NaCl	298	LLE	10	1.00	Roy et al. (2007)
3-methyl-2-butanone, propanoic acid	CH_n, COOH, CH_nCO	NaCl	298	LLE	10	1.00	Roy et al. (2007)
2-butanone	CH_n, CH_nCO	NaCl	298	LLE	9	1.00	Li et al. (1995)
acetone	CH_n, CH_nCO	NaCl	293	SLE	4	1.00	Jurkiewicz (2007)
2-butanone	CH_n, CH_nCO	NaCl	293	SLE	1	1.00	Jurkiewicz (2007)
4-methyl-2-pentanone	CH_n, CH_nCO	NaCl	298	LLE	4	1.00	Schunk et al. (2004)
acetone	CH_n, CH_nCO	NaCl	298	LLE	8	1.00	Marcilla et al. (1995)
acetone	CH_n, CH_nCO	NaCl	298	SLE	13	1.00	Marcilla et al. (1995)
acetone, 1-butanol	CH_n, CH_nCO, OH	NaCl	293	LLE	6	0.80	Santos et al. (2001)
acetone, 1-butanol	CH_n, CH_nCO, OH	NaCl	298	LLE	18	0.80	Olaya et al. (1996)
acetone, 1-butanol	CH_n, CH_nCO, OH	NaCl	298	LLE	7	0.80	Olaya et al. (1996)
acetone, 1-butanol	CH_n, CH_nCO, OH	NaCl	298	SLE	7	1.00	Olaya et al. (1996)
acetone, ethanol	CH_n, CH_nCO, OH	NaCl	298	LLE	9	0.80	Marcilla et al. (1995)
acetone	CH_n, CH_nCO	NaCl	313	VLE(org)	6	0.10	Falabella et al. (2006)
2-butanone	CH_n, CH_nCO	NaCl	313	VLE(org)	6	0.10	Falabella et al. (2006)
2-pentanone	CH_n, CH_nCO	NaCl	313	VLE(org)	6	0.10	Falabella et al. (2006)

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Table 2. Continued.

Organic compounds [a]	Org. main groups	Inorg. salts/acids	T (K)	Data type [b]	N_d	w_d^{init}	Reference
2-hexanone	CH_n, CH_nCO	NaCl	313	VLE(org)	6	0.10	Falabella et al. (2006)
2-heptanone	CH_n, CH_nCO	NaCl	313	VLE(org)	6	0.10	Falabella et al. (2006)
4-methyl-2-pentanone, propanoic acid	CH_n, COOH, CH_nCO	NaNO$_3$	308	LLE	30	1.00	Govindarajan and Sabarathinam (1997)
4-methyl-2-pentanone, butanoic acid	CH_n, COOH, CH_nCO	NaNO$_3$	308	LLE	15	1.00	Govindarajan and Sabarathinam (1997)
4-methyl-2-pentanone, acetic acid	CH_n, COOH, CH_nCO	NaNO$_3$	308	LLE	26	1.00	Govindarajan and Sabarathinam (1995)
4-methyl-2-pentanone	CH_n, CH_nCO	NaNO$_3$	298	LLE	4	1.00	Schunk et al. (2004)
acetone	CH_n, CH_nCO	NaNO$_3$	313	SLE	9	0.50	Bathrick (1896)
acetone	CH_n, CH_nCO	NaNO$_3$	303	SLE	10	0.50	Taylor (1897)
water + ether + salt/acid systems							
2-methoxy-2-methylpropane	CH_n, CH_nO	CaCl$_2$	298	LLE	6	1.00	Salabat (2007)
1,4-dioxane	CH_n, CH_nO	CaCl$_2$	298	LLE	4	1.00	Bogardus and Lynch (1943)
tetrahydrofuran	CH_n, CH_nO	CaCl$_2$	336–338	VLE	17	0.20	Sada et al. (1975b)
1,4-dioxane	CH_n, CH_nO	HCl	298	LLE	5	0.20	Robinson and Selkirk (1948)
2-methoxyethanol	CH_n, CH_nO, OH	KBr	298	SLE	6	1.00	Chiavone-Filho and Rasmussen (1993)
2-butoxyethanol	CH_n, CH_nO, OH	KBr	298	SLE	4	1.00	Chiavone-Filho and Rasmussen (1993)
1,4-dioxane	CH_n, CH_nO	KBr	298	SLE	3	1.00	Herz and Lorentz (1929)
2-methoxy-2-methylpropane	CH_n, CH_nO	KCl	298	LLE	6	1.00	Salabat (2007)
2-methoxyethanol	CH_n, CH_nO, OH	KCl	298	SLE	6	1.00	Chiavone-Filho and Rasmussen (1993)
2-ethoxyethanol	CH_n, CH_nO, OH	KCl	298	SLE	6	1.00	Chiavone-Filho and Rasmussen (1993)
1-methoxy-2-propanol	CH_n, CH_nO, OH	KCl	298	SLE	6	1.00	Chiavone-Filho and Rasmussen (1993)
2-isopropoxyethanol	CH_n, CH_nO, OH	KCl	298	SLE	6	1.00	Chiavone-Filho and Rasmussen (1993)
1,4-dioxane	CH_n, CH_nO	KCl	298	SLE	11	1.00	Eysseltova and Malkova (2006)
1,4-dioxane	CH_n, CH_nO	KCl	298	SLE	5	1.00	Herz and Lorentz (1929)
1,4-dioxane	CH_n, CH_nO	LiCl	298	SLE	4	0.02	Lynch (1942)
1,4-dioxane	CH_n, CH_nO	LiCl	298	SLE	6	0.02	Lynch (1942)
tetrahydrofuran	CH_n, CH_nO	LiCl	336–339	VLE	20	0.20	Sada et al. (1975b)
2-methoxy-2-methylpropane	CH_n, CH_nO	MgCl$_2$	298	LLE	6	1.00	Salabat (2007)
2-methoxy-2-methylpropane	CH_n, CH_nO	NaCl	298	LLE	6	1.00	Salabat (2007)
2-butoxyethanol	CH_n, CH_nO, OH	NaCl	298	SLE	6	1.00	Raridon and Kraus (1971)
2-ethoxyethanol	CH_n, CH_nO, OH	NaCl	298	SLE	6	1.00	Raridon and Kraus (1971)
2-(2-ethoxyethoxy)ethanol	CH_n, CH_nO, OH	NaCl	298	SLE	6	1.00	Raridon and Kraus (1971)
2-methoxyethanol	CH_n, CH_nO, OH	NaCl	298	SLE	6	1.00	Raridon and Kraus (1971)
2-(2-methoxyethoxy)ethanol	CH_n, CH_nO, OH	NaCl	298	SLE	6	1.00	Raridon and Kraus (1971)
1-(2-methoxypropoxy)-2-propanol	CH_n, CH_nO, OH	NaCl	298	SLE	6	1.00	Raridon and Kraus (1971)
2-methoxypropanol	CH_n, CH_nO, OH	NaCl	298	SLE	6	1.00	Raridon and Kraus (1971)
acetic acid, 2-methoxy-2-methylpropane	CH_n, COOH, CH_nO	NaCl	298	LLE	24	0.10	Zhang and Wang (2009)
1,4-dioxane	CH_n, CH_nO	NaCl	298	SLE	6	1.00	Eysseltova and Malkova (2006)
tetrahydrofuran	CH_n, CH_nO	NaCl	336–338	VLE	12	0.20	Sada et al. (1975b)
1,4-dioxane	CH_n, CH_nO	NaCl	298	SLE	3	1.00	Herz and Lorentz (1929)
1,4-dioxane	CH_n, CH_nO	NaNO$_3$	298	SLE	18	1.00	Selikson and Ricci (1942)
1,4-dioxane	CH_n, CH_nO	NH$_4$Cl	298	SLE	3	0.50	Herz and Lorentz (1929)
water + ester + salt/acid systems							
ethyl acetate, ethanol	CH_n, CCOO	CaCl$_2$	298	LLE	26	1.00	Kumagae et al. (1994)
ethyl acetate	CH_n, CCOO	CaCl$_2$	298	LLE	12	1.00	Kumagae et al. (1994)
ethyl acetate	CH_n, CCOO	CaCl$_2$	313	LLE	4	0.80	Lin et al. (2005)
ethyl acetate, ethanol	CH_n, CCOO, OH	CaCl$_2$	283	LLE	8	0.80	Lin et al. (2005)
ethyl acetate, ethanol	CH_n, CCOO, OH	CaCl$_2$	313	LLE	8	0.80	Lin et al. (2005)
ethyl acetate	CH_n, CCOO	CaCl$_2$	344–348	VLE	14	0.50	Rajendran et al. (1991)
ethyl acetate	CH_n, CCOO	KBr	303	solubil.	4	1.00	Altshuller and Everson (1953)
ethyl acetate	CH_n, CCOO	KCl	298	solubil.	4	1.00	Altshuller and Everson (1953)
ethyl acetate	CH_n, CCOO	LiBr	298	solubil.	4	1.00	Altshuller and Everson (1953)
ethyl acetate	CH_n, CCOO	LiCl	298	LLE	11	1.00	Al-Sahhaf et al. (1999)

Table 2. Continued.

Organic compounds [a]	Org. main groups	Inorg. salts/acids	T (K)	Data type [b]	N_d	w_d^{init}	Reference
ethyl acetate	CH$_n$, CCOO	LiCl	298	solubil.	4	1.00	Altshuller and Everson (1953)
ethyl acetate, ethanol (water-free)	CH$_n$, CCOO, OH	LiNO$_3$	345–356	VLE	76	0.50	Topphoff et al. (2001)
ethyl acetate	CH$_n$, CCOO	Na$_2$SO$_4$	303	LLE	4	1.00	Nakamura (1969)
ethyl acetate	CH$_n$, CCOO	NaBr	298	LLE	10	1.00	Al-Sahhaf et al. (1999)
ethyl acetate	CH$_n$, CCOO	NaBr	298	solubil.	4	1.00	Altshuller and Everson (1953)
ethyl acetate	CH$_n$, CCOO	NaCl	303	LLE	5	1.00	Gomis et al. (1993)
methyl acetate	CH$_n$, CCOO	NaCl	298	solubil.	4	1.00	Segatin and Klofutar (2000)
ethyl acetate	CH$_n$, CCOO	NaCl	298	solubil.	4	1.00	Segatin and Klofutar (2000)
1-propyl acetate	CH$_n$, CCOO	NaCl	298	solubil.	4	1.00	Segatin and Klofutar (2000)
1-butyl acetate	CH$_n$, CCOO	NaCl	298	solubil.	4	1.00	Segatin and Klofutar (2000)
isobutyl acetate	CH$_n$, CCOO	NaCl	298	solubil.	4	1.00	Segatin and Klofutar (2000)
2-butyl acetate	CH$_n$, CCOO	NaCl	298	solubil.	4	1.00	Segatin and Klofutar (2000)
tert-butyl acetate	CH$_n$, CCOO	NaCl	298	solubil.	4	1.00	Segatin and Klofutar (2000)
1-pentyl acetate	CH$_n$, CCOO	NaCl	298	solubil.	4	1.00	Segatin and Klofutar (2000)
1-hexyl acetate	CH$_n$, CCOO	NaCl	298	solubil.	4	1.00	Segatin and Klofutar (2000)
ethyl acetate	CH$_n$, CCOO	NaCl	298	solubil.	4	1.00	Altshuller and Everson (1953)
ethyl acetate	CH$_n$, CCOO	NaCl	344–347	VLE	14	0.50	Rajendran et al. (1991)
water + multifunctional aromatic compounds + salt/acid systems							
benzene	ACH$_n$	(NH$_4$)$_2$SO$_4$	293	LLE	4	1.00	van Delden et al. (2004)
benzene	ACH$_n$	(NH$_4$)$_2$SO$_4$	313	LLE	4	0.80	van Delden et al. (2004)
2,4-dihydroxybenzaldehyde	ACH$_n$, ACOH, CHO	Ca(NO$_3$)$_2$	298	SLE	4	1.00	this study
benzene	ACH$_n$	CaCl$_2$	303	solubil.	5	0.80	Boddu et al. (2001)
benzene	ACH$_n$	H$_2$SO$_4$	303	solubil.	7	0.20	Hanson and Ismail (1975)
benzene	ACH$_n$	HCl	298	solubil.	4	1.00	McDevit and Long (1952)
phenol	ACH$_n$, ACOH	HCl	300	solubil.	1	1.00	Jaoui et al. (2002)
benzene	ACH$_n$	HCl	303	LLE	8	0.00	Ishidao et al. (2001)
phenol	ACH$_n$, ACOH	HCl	285	LLE	10	0.80	Schreinemakers and van den Bos (1912)
phenol	ACH$_n$, ACOH	HCl	298	$\gamma_\pm$	27	2.00	Sadek et al. (1972)
benzene	ACH$_n$	HNO$_3$	295	solubil.	6	0.50	Hanson and Ismail (1975)
2-hydroxybenzoic acid	ACH$_n$, ACOH, COOH	K$_2$SO$_4$	298	SLE	1	1.00	Sugunan and Thomas (1995)
2-hydroxybenzoic acid	ACH$_n$, ACOH, COOH	K$_2$SO$_4$	308	SLE	8	0.50	Sugunan and Thomas (1995)
4-hydroxybenzoic acid	ACH$_n$, ACOH, COOH	K$_2$SO$_4$	298	SLE	1	1.00	Sugunan and Thomas (1995)
4-hydroxybenzoic acid	ACH$_n$, ACOH, COOH	K$_2$SO$_4$	308	SLE	8	0.20	Sugunan and Thomas (1995)
benzene	ACH$_n$	KBr	298	solubil.	2	1.00	McDevit and Long (1952)
2-hydroxybenzoic acid	ACH$_n$, ACOH, COOH	KBr	298	SLE	3	1.00	Osol and Kilpatrick (1933)
2-hydroxybenzoic acid	ACH$_n$, ACOH, COOH	KBr	298	SLE	1	1.00	Sugunan and Thomas (1995)
2-hydroxybenzoic acid	ACH$_n$, ACOH, COOH	KBr	308	SLE	8	0.50	Sugunan and Thomas (1995)
4-hydroxybenzoic acid	ACH$_n$, ACOH, COOH	KBr	298	SLE	1	1.00	Sugunan and Thomas (1995)
4-hydroxybenzoic acid	ACH$_n$, ACOH, COOH	KBr	308	SLE	8	0.50	Sugunan and Thomas (1995)
protocatechuic acid	ACH$_n$, ACOH, COOH	KCl	298	SLE	7	1.00	Noubigh et al. (2007b)
vanillin	ACH$_n$, ACOH, CH$_n$O, CHO	KCl	298	SLE	7	1.00	Noubigh et al. (2007b)
vanillic acid	ACH$_n$, ACOH, CH$_n$O, COOH	KCl	298	SLE	6	1.00	Noubigh et al. (2007b)
gallic acid	ACH$_n$, ACOH, COOH	KCl	298	SLE	7	1.00	Noubigh et al. (2007b)
ferulic acid	ACH$_n$, ACOH, CH$_n$O, C=C, COOH	KCl	298	SLE	7	1.00	Noubigh et al. (2007a)
syringic acid	ACH$_n$, ACOH, CH$_n$O, COOH	KCl	298	SLE	7	1.00	Noubigh et al. (2007a)
benzene	ACH$_n$	KCl	298	solubil.	2	1.00	McDevit and Long (1952)
2-hydroxybenzoic acid	ACH$_n$, ACOH, COOH	KCl	298	SLE	5	1.00	Osol and Kilpatrick (1933)
3-hydroxybenzoic acid	ACH$_n$, ACOH, COOH	KCl	298	SLE	5	1.00	Osol and Kilpatrick (1933)
4-hydroxybenzoic acid	ACH$_n$, ACOH, COOH	KCl	298	SLE	7	1.00	Osol and Kilpatrick (1933)
2-hydroxybenzoic acid	ACH$_n$, ACOH, COOH	KCl	298	SLE	1	1.00	Sugunan and Thomas (1995)
2-hydroxybenzoic acid	ACH$_n$, ACOH, COOH	KCl	308	SLE	8	0.50	Sugunan and Thomas (1995)
4-hydroxybenzoic acid	ACH$_n$, ACOH, COOH	KCl	298	SLE	1	1.00	Sugunan and Thomas (1995)
4-hydroxybenzoic acid	ACH$_n$, ACOH, COOH	KCl	308	SLE	8	0.50	Sugunan and Thomas (1995)
2-hydroxybenzoic acid	ACH$_n$, ACOH, COOH	KNO$_3$	298	SLE	1	1.00	Sugunan and Thomas (1995)
2-hydroxybenzoic acid	ACH$_n$, ACOH, COOH	KNO$_3$	308	SLE	8	0.50	Sugunan and Thomas (1995)

Table 2. Continued.

Organic compounds [a]	Org. main groups	Inorg. salts/acids	T (K)	Data type [b]	N_d	w_d^{init}	Reference
protocatechuic acid	ACH_n, ACOH, COOH	LiCl	298	SLE	7	1.00	Noubigh et al. (2007b)
vanillin	ACH_n, ACOH, CH_nO, CHO	LiCl	298	SLE	7	1.00	Noubigh et al. (2007b)
vanillic acid	ACH_n, ACOH, CH_nO, COOH	LiCl	298	SLE	7	1.00	Noubigh et al. (2007b)
gallic acid	ACH_n, ACOH, COOH	LiCl	298	SLE	7	1.00	Noubigh et al. (2007b)
ferulic acid	ACH_n, ACOH, CH_nO, C=C, COOH	LiCl	298	SLE	7	1.00	Noubigh et al. (2007a)
syringic acid	ACH_n, ACOH, CH_nO, COOH	LiCl	298	SLE	7	1.00	Noubigh et al. (2007a)
benzene	ACH_n	LiCl	298	solubil.	2	1.00	McDevit and Long (1952)
2-hydroxybenzoic acid	ACH_n, ACOH, COOH	LiCl	298	SLE	4	1.00	Osol and Kilpatrick (1933)
2,4-dihydroxybenzaldehyde	ACH_n, ACOH, CHO	$Mg(NO_3)_2$	298	SLE	4	1.00	this study
2-hydroxybenzoic acid	ACH_n, ACOH, COOH	$MgSO_4$	298	SLE	1	1.00	Sugunan and Thomas (1995)
2-hydroxybenzoic acid	ACH_n, ACOH, COOH	$MgSO_4$	308	SLE	8	1.00	Sugunan and Thomas (1995)
4-hydroxybenzoic acid	ACH_n, ACOH, COOH	$MgSO_4$	298	SLE	1	0.20	Sugunan and Thomas (1995)
4-hydroxybenzoic acid	ACH_n, ACOH, COOH	$MgSO_4$	308	SLE	8	0.20	Sugunan and Thomas (1995)
benzene	ACH_n	Na_2SO_4	298	solubil.	3	1.00	McDevit and Long (1952)
gallic acid	ACH_n, ACOH, COOH	Na_2SO_4	298	SLE	3	1.00	Noubigh et al. (2008)
syringic acid	ACH_n, ACOH, CH_nO, COOH	Na_2SO_4	298	SLE	3	1.00	Noubigh et al. (2008)
protocatechuic acid	ACH_n, ACOH, COOH	Na_2SO_4	298	SLE	3	1.00	Noubigh et al. (2008)
vanillin	ACH_n, ACOH, CH_nO, CHO	Na_2SO_4	298	SLE	3	1.00	Noubigh et al. (2008)
2,4-dihydroxybenzaldehyde	ACH_n, ACOH, CHO	Na_2SO_4	298	SLE	3	1.00	this study
benzene	ACH_n	NaBr	298	solubil.	3	1.00	McDevit and Long (1952)
protocatechuic acid	ACH_n, ACOH, COOH	NaCl	298	SLE	8	1.00	Noubigh et al. (2007b)
vanillin	ACH_n, ACOH, CH_nO, CHO	NaCl	298	SLE	8	1.00	Noubigh et al. (2007b)
vanillic acid	ACH_n, ACOH, CH_nO, COOH	NaCl	298	SLE	7	1.00	Noubigh et al. (2007b)
gallic acid	ACH_n, ACOH, COOH	NaCl	298	SLE	7	1.00	Noubigh et al. (2007b)
ferulic acid	ACH_n, ACOH, CH_nO, C=C, COOH	NaCl	298	SLE	7	1.00	Noubigh et al. (2007a)
syringic acid	ACH_n, ACOH, CH_nO, COOH	NaCl	298	SLE	7	1.00	Noubigh et al. (2007a)
benzene	ACH_n	NaCl	298	solubil.	4	1.00	McDevit and Long (1952)
2-hydroxybenzoic acid	ACH_n, ACOH, COOH	NaCl	298	SLE	4	1.00	Osol and Kilpatrick (1933)
phthalic acid	ACH_n, COOH	NaCl	298	SLE	13	1.00	Bretti et al. (2005)
phenol	ACH_n, ACOH	NaCl	300	solubil.	1	1.00	Bretti et al. (2005)
2,4-dihydroxybenzaldehyde	ACH_n, ACOH, CHO	NaCl	298	SLE	4	1.00	this study
benzene	ACH_n	$NaNO_3$	298	solubil.	3	1.00	McDevit and Long (1952)
2,4-dihydroxybenzaldehyde	ACH_n, ACOH, CHO	NH_4Br	298	SLE	3	1.00	this study
benzene	ACH_n	NH_4Cl	298	solubil.	3	1.00	McDevit and Long (1952)

[a] Unless stated otherwise, the mixtures contain water as additional component.

[b] The different data types as described in Sect. 4. "VLE" indicates complete x-y-T-p VLE data, "VLE(org)" are organic VLE data from Henry's constant measurements, "solubil." refers to liquid-liquid solubility limit data of organic compounds, and "SEDB" denotes the scanning EDB method.

Extended parameterization of the AIOMFAC model

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Conclusions | References

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Table 3. Selected properties of organic compounds used for the middle-range parameterization of organic main group ↔ ion interactions.

Organic compound	Chemical formula (subgroups) [a]	M (kg mol^{-1}) [b]	O : C ratio	Structure
alcohols/polyols/sugars				
ethanol	$(CH_3)(CH_2)(OH)$	0.046068	0.500	
1-propanol	$(CH_3)(CH_2)_2(OH)$	0.060095	0.333	
2-propanol (isopropanol)	$(CH_3)_2(CH)(OH)$	0.060095	0.333	
1-butanol	$(CH_3)(CH_2)_3(OH)$	0.074122	0.250	
2-butanol	$(CH_3)_2(CH_2)(CH)(OH)$	0.074122	0.250	
isobutanol	$(CH_3)_2(CH)(CH_2)(OH)$	0.074122	0.250	
tert-butanol (2-methyl-2-propanol)	$(CH_3)_3(C)(OH)$	0.074122	0.250	
2-methyl-1-butanol	$(CH_3)_2(CH_2)_2(CH)(OH)$	0.088148	0.200	
2-methyl-2-butanol	$(CH_3)_3(CH_2)(C)(OH)$	0.088148	0.200	
1-pentanol	$(CH_3)(CH_2)_4(OH)$	0.088148	0.200	
2-pentanol	$(CH_3)_2(CH_2)_2(CH)(OH)$	0.088148	0.200	
3-pentanol	$(CH_3)_2(CH_2)_2(CH)(OH)$	0.088148	0.200	
3-methyl-1-butanol (Isopentanol)	$(CH_3)_2(CH)(CH_2)_2(OH)$	0.088148	0.200	
1-hexanol	$(CH_3)(CH_2)_5(OH)$	0.102175	0.167	
1,2-ethanediol (ethylene glycol)	$(CH_2)_2(OH)_2$	0.062068	1.000	
glycerol	$(CH_2)_2(CH)(OH)_3$	0.092094	1.000	
1,4-butanediol	$(CH_2)_4(OH)_2$	0.090121	0.500	
1,2-butanediol	$(CH_3)(CH_2)_2(CH)(OH)_2$	0.090121	0.500	
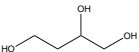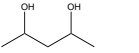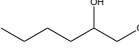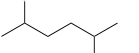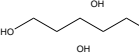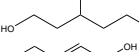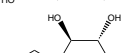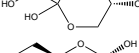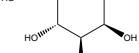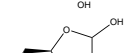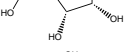
Table 3. Continued.

Organic compound	Chemical formula (subgroups) [a]	M (kg mol^{-1}) [b]	O : C ratio	Structure
1,2,4-butanetriol	$(CH_2)_3(CH)(OH)_3$	0.106120	0.750	
2,4-pentanediol	$(CH_3)_2(CH_2)(CH)_2(OH)_2$	0.104148	0.400	
1,2-hexanediol	$(CH_3)(CH_2)_4(CH)(OH)_2$	0.118174	0.333	
2,5-hexanediol	$(CH_3)_2(CH_2)_2(CH)_2(OH)_2$	0.118174	0.333	
1,7-heptanediol	$(CH_2)_7(OH)_2$	0.132201	0.286	
1,3-nonanediol	$(CH_3)(CH_2)_7(CH)(OH)_2$	0.160254	0.222	
1,4-dihydroxy-2-butene	$(OH)_2(CH_2)_2(CH=CH)$	0.088105	0.500	
D-fructopyranose (dissolved D-fructose)	$(CH_2)(CH)_3(C)(OH)_5(CH_2O)$	0.180156	1.000	
D-mannopyranose (dissolved D-mannose)	$(CH_2)(CH)_4(OH)_5(CHO)$	0.180156	1.000	
D-ribofuranose (dissolved D-ribose)	$(CH_2)(CH)_3(OH)_4(CHO)$	0.150130	1.000	
levoglucosan	$(CH)_4(OH)_3(CH_2O)(CHO)$	0.162096	0.833	
carboxylic acids				
formic acid	$(HCOOH)$	0.046025	2.000	
acetic acid	$(CH_3)(COOH)$	0.060052	1.000	
propanoic acid (propionic acid)	$(CH_3)(CH_2)(COOH)$	0.074079	0.667	

Extended parameterization of the AIOMFAC model
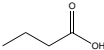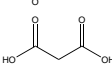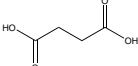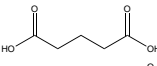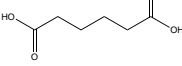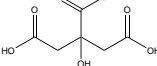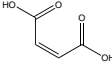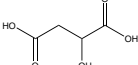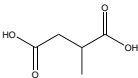
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Table 3. Continued.

Organic compound	Chemical formula (subgroups) [a]	M (kg mol^{-1}) [b]	O : C ratio	Structure
butanoic acid (butyric acid)	$(CH_3)(CH_2)_2(COOH)$	0.088105	0.500	
2-methylpropanoic acid (isobutyric acid)	$(CH_3)_2(CH)(COOH)$	0.088105	0.500	
methacrylic acid (2-methyl-2-propenoic acid)	$(CH_3)(CH_2=C)(COOH)$	0.086089	0.500	
oxalic acid	$(COOH)_2$	0.090035	2.000	
malonic acid	$(CH_2)(COOH)_2$	0.104026	1.333	
succinic acid	$(CH_2)_2(COOH)_2$	0.118052	1.000	
glutaric acid	$(CH_2)_3(COOH)_2$	0.132078	0.800	
adipic acid	$(CH_2)_4(COOH)_2$	0.146141	0.667	
citric acid	$(CH_2)_2(C)(OH)(COOH)_3$	0.192124	1.167	
maleic acid	$(CH=CH)(COOH)_2$	0.116072	1.000	
malic acid	$(CH_2)(CH)(OH)(COOH)_2$	0.134087	1.250	
methylsuccinic acid	$(CH_2)(CH)(CH_3)(COOH)_2$	0.132115	0.800	

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Table 3. Continued.

Organic compound	Chemical formula (subgroups) [a]	M (kg mol^{-1}) [b]	O : C ratio	Structure
2-methylglutaric acid	$(CH_2)_2(CH)(CH_3)$ $(COOH)_2$	0.146141	0.667	
3-methylglutaric acid	$(CH_2)_2(CH)(CH_3)$ $(COOH)_2$	0.146141	0.667	
2,2-dimethylsuccinic acid	$(CH_2)(C)(CH_3)_2$ $(COOH)_2$	0.146141	0.667	
ketones				
acetone (dimethylketone, 2-propanone)	$(CH_3CO)(CH_3)$	0.058079	0.333	
2-butanone (methyl ethyl ketone)	$(CH_3CO)(CH_2)$ (CH_3)	0.072106	0.250	
3-methyl-2-butanone (isopropyl methyl ketone)	$(CH_3)_2(CH)$ (CH_3CO)	0.086132	0.200	
2-pentanone	$(CH_3CO)(CH_2)_2$ (CH_3)	0.086132	0.200	
4-methyl-2-pentanone (methyl isobutyl ketone)	$(CH_3)_2(CH)$ $(CH_2)(CH_3CO)$	0.100159	0.167	
diethylketone (3-pentanone)	$(CH_3)_2(CH_2)$ (CH_2CO)	0.086132	0.200	
2-hexanone	$(CH_3CO)(CH_2)_3$ (CH_3)	0.100159	0.167	
2-heptanone	$(CH_3CO)(CH_2)_4$ (CH_3)	0.114185	0.143	
3-heptanone	$(CH_2CO)(CH_2)_3$ $(CH_3)_2$	0.114185	0.143	
ethers/ether-alcohols				
2-methoxy-2-methylpropane (methyl *tert*-butyl ether)	$(CH_3)_3(C)(CH_3O)$	0.088148	0.200	
2-methoxyethanol	$(CH_2)_2(OH)$ (CH_3O)	0.076094	0.667	
2-ethoxyethanol	$(CH_3)(CH_2)_2$ $(OH)(CH_2O)$	0.090121	0.500	
1-methoxy-2-propanol	$(CH_3)(CH)(OH)$ $(CH_2)(CH_3O)$	0.090121	0.500	

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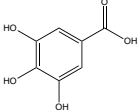Conclusions | References

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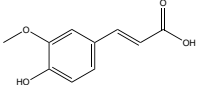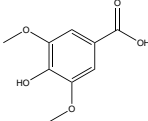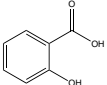|◄ | ►|

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Table 3. Continued.

Organic compound	Chemical formula (subgroups) [a]	M (kg mol^{-1}) [b]	O : C ratio	Structure
2-isopropoxyethanol	(CH$_3$)$_2$(CH)(CH$_2$O) (CH$_2$)(OH)	0.104148	0.400	
2-butoxyethanol	(CH$_3$)(CH$_2$)$_4$ (CH$_2$O)(OH)	0.118174	0.333	
2-(2-ethoxyethoxy)ethanol (carbitol)	(CH$_3$)(CH$_2$)$_3$ (CH$_2$O)$_2$(OH)	0.134174	0.500	
2-(2-methoxyethoxy)ethanol (methyl carbitol)	(CH$_3$)(CH$_2$)$_2$ (CH$_2$O)$_2$(OH)	0.120147	0.600	
2-methoxypropanol	(CH$_3$)(CH)(CH$_3$O) (CH$_2$)(OH)	0.090121	0.500	
1-(2-methoxypropoxy)-2-propanol	(CH$_3$)$_2$(CH)$_2$(CH$_3$O) (CH$_2$)(CH$_2$O)(OH)	0.148200	0.429	
tetrahydrofuran	(CH$_2$)$_3$(CH$_2$O)	0.072106	0.250	
1,4-dioxane (dioxoethylene ether)	(CH$_2$O)$_2$(CH$_2$)$_2$	0.088105	0.500	
esters				
methyl acetate	(CH$_3$COO)(CH$_3$)	0.074079	0.667	
ethyl acetate	(CH$_3$COO)(CH$_2$) (CH$_3$)	0.088105	0.500	
1-propyl acetate	(CH$_3$COO)(CH$_2$)$_2$ (CH$_3$)	0.102132	0.400	
1-butyl acetate	(CH$_3$COO)(CH$_2$)$_3$ (CH$_3$)	0.116158	0.333	
isobutyl acetate	(CH$_3$COO)(CH$_2$) (CH)(CH$_3$)$_2$	0.116158	0.333	
2-butyl acetate	(CH$_3$COO)(CH) (CH$_2$)(CH$_3$)$_2$	0.116158	0.333	
tert-butyl acetate	(CH$_3$COO) (C)(CH$_3$)$_3$	0.116158	0.333	
1-pentyl acetate	(CH$_3$COO) (CH$_2$)$_4$(CH$_3$)	0.130185	0.286	
1-hexyl acetate	(CH$_3$COO) (CH$_2$)$_5$(CH$_3$)	0.144211	0.250	

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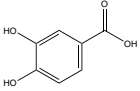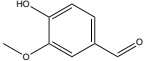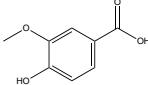
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Table 3. Continued.

Organic compound	Chemical formula (subgroups) [a]	M (kg mol^{-1}) [b]	O : C ratio	Structure
multifunctional aromatic compounds				
benzene	(ACH)$_6$	0.078112	0.000	
phenol	(ACH)$_5$(ACOH)	0.094111	0.167	
protocatechuic acid	(ACH)$_3$(AC) (ACOH)$_2$(COOH)	0.154120	0.571	
vanillin	(ACH)$_3$(AC)$_2$(ACOH) (CHO)(CH$_3$O)	0.152147	0.375	
vanillic acid	(ACH)$_3$(AC)$_2$ (ACOH)(COOH)(CH$_3$O)	0.168147	0.500	
gallic acid	(ACH)$_2$(AC) (ACOH)$_3$(COOH)	0.170120	0.714	
ferulic acid	(ACH)$_3$(AC)$_2$(ACOH) (CH$_3$O)(CH=CH)(COOH)	0.194184	0.400	
syringic acid	(ACH)$_2$(AC)$_3$(ACOH) (CH$_3$O)$_2$(COOH)	0.198173	0.556	
salicylic acid	(ACH)$_4$(AC)(ACOH) (COOH)	0.138121	0.429	

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Table 3. Continued.

Organic compound	Chemical formula (subgroups) [a]	M (kg mol^{-1}) [b]	O : C ratio	Structure
3-hydroxybenzoic acid	(ACH)$_4$(AC) (ACOH)(COOH)	0.138121	0.429	
4-hydroxybenzoic acid	(ACH)$_4$(AC) (ACOH)(COOH)	0.138121	0.429	
phthalic acid	(ACH)$_4$(AC)$_2$ (COOH)$_2$	0.166131	0.500	
2,4-dihydroxybenzaldehyde	(ACH)$_4$(ACOH)$_2$(CHO)	0.138121	0.429	

[a] The brackets distinguish different functional subgroups, sectioning the molecules according to the nomenclature of UNIFAC/AIOMFAC. Note that the UNIFAC parameters of Marcolli and Peter (2005) are used for hydroxyl groups and associated alkyl groups, i.e., the alkyl subgroups in alcohols are further distinguished into CH$_n$ [in hydrophobic tails of alcohols], CH$_n$ [in alcohols], and CH$_n^{(OH)}$ [with hydroxyl group] (where n = 0,1,2,3), as indicated in Fig. 1. UNIFAC parameters of Peng et al. (2001) are applied for the COOH group and its interactions with the functional group OH and with H$_2$O (see Fig. 1 and Sec. 3.1).

[b] Molar mass of the compound's natural isotope mixture.

Table 4. Data types, number of data points (N_d), initial weighting (w_d^{init}), and sources of experimental data of binary aqueous CaBr$_2$, MgBr$_2$, CaSO$_4$, and H$_2$SO$_4$ systems, aqueous multi-salt mixtures at SLE of CaSO$_4 \cdot$2H$_2$O (gypsum), and mixtures of H$_2$SO$_4$ and (NH$_4$)$_2$SO$_4$ at various molar mixing ratios as specified in brackets.

Solvent	Electrolytes	T (K)	Data type [a]	N_d	w_d^{init}	Reference
water	CaBr$_2$	298	$\gamma_\pm$	15	2.00	Zaytsev and Aseyev (1992)
water	CaBr$_2$	298	$\gamma_\pm$	23	2.00	Robinson and Stokes (2002)
water	CaBr$_2$	298	a_w(bulk)	23	2.00	Robinson and Stokes (2002)
water	MgBr$_2$	298	$\gamma_\pm$	15	2.00	Zaytsev and Aseyev (1992)
water	MgBr$_2$	298	$\gamma_\pm$	21	2.00	Robinson and Stokes (2002)
water	MgBr$_2$	298	a_w(bulk)	21	2.00	Robinson and Stokes (2002)
water	CaSO$_4$	298	$\gamma_\pm$	7	2.00	Lilley and Briggs (1976)
water	CaSO$_4$	298	$\gamma_\pm$	20	2.00	Malatesta and Zamboni (1997)
water	CaSO$_4$, Na$_2$SO$_4$	313	SLE	12	1.00	Barba et al. (1984)
water	CaSO$_4$, Na$_2$SO$_4$, MgCl$_2$	313	SLE	34	1.00	Barba et al. (1984)
water	CaSO$_4$, NaCl	308	SLE	13	1.00	Kumar et al. (2007)
water	CaSO$_4$, NaCl, CaCl$_2$	308	SLE	32	1.00	Kumar et al. (2007)
water	H$_2$SO$_4$	298	a_w(bulk)	64	2.00	Robinson and Stokes (2002)
water	H$_2$SO$_4$	298	a_w(bulk)	81	2.00	Staples (1981)
water	H$_2$SO$_4$	298	$\alpha_{\text{HSO}_4^-}$	4	0.20	Knopf et al. (2003)
water	H$_2$SO$_4$	298	$\alpha_{\text{HSO}_4^-}$	11	0.20	Myhre et al. (2003)
water	(NH$_4$)$_2$SO$_4$, H$_2$SO$_4$ [1 : 1] (= NH$_4$HSO$_4$)	298	$\alpha_{\text{HSO}_4^-}$	9	0.20	Young et al. (1959)
water	(NH$_4$)$_2$SO$_4$, H$_2$SO$_4$ [1 : 1]	298	$\alpha_{\text{HSO}_4^-}$	7	0.20	Dawson et al. (1986)
water	(NH$_4$)$_2$SO$_4$, H$_2$SO$_4$ [1 : 1]	298	a_w(bulk)	12	2.00	Tang and Munkelwitz (1977)
water	(NH$_4$)$_2$SO$_4$, H$_2$SO$_4$ [1 : 1]	298	a_w(EDB)	40	1.00	Spann (1984)
water	(NH$_4$)$_2$SO$_4$, H$_2$SO$_4$ [1 : 1]	298	a_w(EDB)	23	1.00	Kim et al. (1994)
water	(NH$_4$)$_2$SO$_4$, H$_2$SO$_4$ [1 : 2]	298	a_w(EDB)	33	1.00	Kim et al. (1994)
water	(NH$_4$)$_2$SO$_4$, H$_2$SO$_4$ [2 : 1]	298	a_w(bulk)	12	2.00	Zuend et al. (2008)
water	(NH$_4$)$_2$SO$_4$, H$_2$SO$_4$ [2 : 1]	298	a_w(EDB)	33	0.50	Zuend et al. (2008)
water	(NH$_4$)$_3$H(SO$_4$)$_2$ [3 : 1]	298	a_w(bulk)	9	2.00	Tang and Munkelwitz (1994)
water	(NH$_4$)$_2$SO$_4$, H$_2$SO$_4$ [0.4824 : 1]	298	a_w(bulk)	36	2.00	Clegg et al. (1996)
water	(NH$_4$)$_2$SO$_4$, H$_2$SO$_4$ [1.9470 : 1]	298	a_w(bulk)	35	2.00	Clegg et al. (1996)
water	NaHSO$_4$	298	a_w(bulk)	32	2.00	Tang and Munkelwitz (1994)

[a] Data type $\alpha_{\text{HSO}_4^-}$ denotes measurement of the degree of dissociation of the bisulfate ion, as described in Zuend et al. (2008).

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Table 5. Fitted binary cation ↔ anion middle-range interaction parameters of new and revised aqueous electrolyte solutions.

c	a	$b_{c,a}^{(1)}$ (kg mol^{-1})	$b_{c,a}^{(2)}$ (kg mol^{-1})	$b_{c,a}^{(3)}$ (kg$^{1/2}$ mol$^{-1/2}$)	$c_{c,a}^{(1)}$ (kg^2 mol^{-2})	$c_{c,a}^{(2)}$ (kg$^{1/2}$ mol$^{-1/2}$)
Ca^{2+}	Br^-	8.90929×10^{-1}	6.10134×10^{-2}	8.00000×10^{-1}	-2.38788×10^{-1}	7.62961×10^{-1}
Mg^{2+}	Br^-	2.60487×10^{-1}	1.01704	8.00000×10^{-1}	6.16264×10^{-2}	2.99475×10^{-1}
Ca^{2+}	SO_4^{2-}	1.29567	-6.96806×10^{-1}	8.00000×10^{-1}	1.59159	2.56217×10^{-1}
H^+	SO_4^{2-}	2.86343×10^{-1}	-5.99615	1.36861	-5.35977×10^{-1}	9.07200×10^{-1}
H^+	HSO_4^-	2.15532×10^{-2}	5.62966×10^{-1}	1.42442×10^{-1}	7.03842×10^{-2}	7.14194×10^{-1}
Na^+	HSO_4^-	1.53214×10^{-2}	4.00000×10^{-1}	4.23635×10^{-1}	3.50072×10^{-3}	4.00000×10^{-1}
NH_4^+	HSO_4^-	7.59735×10^{-3}	1.43012×10^{-1}	2.03954×10^{-1}	6.31184×10^{-3}	8.25386×10^{-1}

Table 6. Fitted special middle-range parameters representing non-zero cation $\leftrightarrow$ cation and cation $\leftrightarrow$ cation $\leftrightarrow$ anion interactions. $R_{c,c'}$ and $Q_{c,c',a}$ parameters of all other ion interactions are set to zero.

c	c'	a	$R_{c,c'}$ (kg mol^{-1})	$Q_{c,c',a}$ (kg^2 mol^{-2})
NH_4^+	H^+		-1.54486×10^{-1}	
NH_4^+	H^+	HSO_4^-		4.48354×10^{-4}

Table 7. Matrix of determined middle-range organic main group ↔ ion interaction parameters $b_{k,i}^{(1)}$ and $b_{k,i}^{(2)}$ used in Eq. (5), organized as in Fig. 8. At each interaction pair entry, upper and lower values are the $b_{k,i}^{(1)}$ (kg mol^{-1}) and $b_{k,i}^{(2)}$ (kg mol^{-1}) parameters, respectively. Parameters $b_{k,i}^{(3)}$ of Eq. (5) are kept constant at 1.2 kg$^{1/2}$ mol$^{-1/2}$ for all interaction pairs. Entry (?) denotes an interaction parameter that has not been determined to date.

k,i	H^+	Li^+	Na^+	K^+	NH_4^+	Mg^{2+}	Ca^{2+}	Cl^-	Br^-	NO_3^-	HSO_4^-	SO_4^{2-}
CH_n	9.44787×10^{-2}	7.96162×10^{-2}	1.05881×10^{-1}	9.83642×10^{-2}	5.66744×10^{-2}	8.76190×10^{-2}	1.02141×10^{-1}	6.91431×10^{-2}	4.13679×10^{-2}	4.23323×10^{-2}	1.24453×10^{-1}	7.59843×10^{-2}
	6.56897×10^{-2}	4.66958×10^{-2}	2.26682×10^{-2}	4.20328×10^{-2}	4.31654×10^{-2}	-2.31755×10^{-2}	7.47421×10^{-2}	5.88900×10^{-2}	3.43938×10^{-2}	4.85325×10^{-2}	1.42679×10^{-1}	1.13096×10^{-1}
$CH_n^{(OH)}$	7.96996×10^{-2}	6.18899×10^{-2}	1.05881×10^{-1}	6.84793×10^{-2}	3.90465×10^{-2}	6.74901×10^{-2}	8.09257×10^{-2}	5.22791×10^{-2}	4.09489×10^{-2}	3.00003×10^{-2}	9.61748×10^{-2}	5.25736×10^{-2}
	3.13421×10^{-2}	2.58311×10^{-2}	9.73093×10^{-3}	3.20716×10^{-2}	4.44483×10^{-2}	-2.23263×10^{-2}	5.92614×10^{-2}	3.65601×10^{-2}	1.68833×10^{-2}	3.96702×10^{-2}	9.75711×10^{-2}	7.93153×10^{-2}
OH	-2.49640×10^{-2}	5.87773×10^{-3}	7.65000×10^{-3}	2.70478×10^{-3}	5.23824×10^{-3}	3.10304×10^{-3}	1.03873×10^{-2}	9.15639×10^{-3}	4.68668×10^{-3}	-2.70727×10^{-2}	-6.10023×10^{-2}	2.27122×10^{-3}
	7.78687×10^{-5}	-5.62998×10^{-2}	-7.48582×10^{-3}	-3.23740×10^{-2}	5.68411×10^{-3}	-8.65932×10^{-3}	-5.46599×10^{-4}	-2.24925×10^{-2}	1.47618×10^{-3}	8.32695×10^{-3}	-3.95218×10^{-2}	1.22439×10^{-2}
$COOH$	-1.54168×10^{-2}	4.45875×10^{-2}	5.55665×10^{-2}	3.24047×10^{-2}	-2.53489×10^{-2}	5.11236×10^{-2}	2.60545×10^{-2}	3.88574×10^{-2}	2.99897×10^{-2}	-2.75568×10^{-3}	7.99946×10^{-2}	-4.48204×10^{-2}
	-7.47215×10^{-5}	-6.96806×10^{-3}	-6.69604×10^{-4}	1.99525×10^{-2}	-3.14902×10^{-2}	-2.49540×10^{-2}	2.33172×10^{-2}	3.00968×10^{-2}	1.23743×10^{-2}	6.66352×10^{-4}	5.62030×10^{-6}	-5.00144×10^{-2}
CH_nCO	1.96849×10^{-1}	1.11797×10^{-1}	1.62860×10^{-1}	1.33560×10^{-1}	9.37140×10^{-2}	1.44219×10^{-1}	2.04458×10^{-1}	1.32956×10^{-1}	6.48040×10^{-2}	4.54274×10^{-2}	(?)	1.23888×10^{-1}
	-4.27577×10^{-3}	1.42257×10^{-1}	5.04545×10^{-2}	5.03945×10^{-2}	5.16922×10^{-2}	-2.09508×10^{-2}	1.52489×10^{-1}	1.36387×10^{-1}	4.15174×10^{-2}	6.62415×10^{-2}	(?)	1.34675×10^{-1}
CHO	(?)	5.18983×10^{-1}	1.05740×10^{-1}	4.74863×10^{-2}	5.62254×10^{-2}	(?)	1.02119×10^{-1}	6.90488×10^{-2}	3.71747×10^{-2}	4.13984×10^{-2}	(?)	3.90486×10^{-2}
	(?)	-1.68243×10^{-3}	2.27265×10^{-2}	1.42102×10^{-2}	3.70256×10^{-2}	(?)	7.47142×10^{-2}	5.88674×10^{-2}	1.80747×10^{-2}	4.87521×10^{-2}	(?)	7.19691×10^{-2}
CH_nO	9.35736×10^{-2}	6.12871×10^{-2}	1.01867×10^{-1}	6.47475×10^{-2}	4.06031×10^{-2}	7.25245×10^{-2}	8.25460×10^{-2}	5.42575×10^{-2}	4.13329×10^{-2}	4.77384×10^{-3}	6.07156×10^{-2}	4.69045×10^{-2}
	6.14536×10^{-2}	2.69698×10^{-2}	1.48542×10^{-2}	6.47239×10^{-2}	4.50589×10^{-2}	-2.34403×10^{-2}	7.07754×10^{-2}	4.16149×10^{-2}	2.39118×10^{-2}	8.52485×10^{-2}	2.43957×10^{-2}	8.60605×10^{-2}
$CCOO$	(?)	1.11797×10^{-1}	1.62860×10^{-1}	1.01841×10^{-1}	(?)	(?)	2.01780×10^{-1}	1.32798×10^{-1}	6.47542×10^{-2}	4.54273×10^{-2}	(?)	1.72676×10^{-2}
	(?)	1.42257×10^{-1}	5.04545×10^{-2}	-4.26811×10^{-3}	(?)	(?)	-1.07750×10^{-1}	1.36298×10^{-1}	4.15094×10^{-2}	6.62415×10^{-2}	(?)	1.07737×10^{-3}
$C=C$	1.98174×10^{-1}	1.28778×10^{-1}	2.18720×10^{-1}	1.59394×10^{-1}	9.38185×10^{-2}	1.46539×10^{-1}	2.06213×10^{-1}	1.32956×10^{-1}	8.22912×10^{-2}	6.70102×10^{-2}	2.29945×10^{-1}	1.24112×10^{-1}
	1.38151×10^{-1}	1.36276×10^{-1}	5.09909×10^{-2}	6.73063×10^{-2}	1.16555×10^{-1}	-1.39578×10^{-1}	1.52563×10^{-1}	1.36387×10^{-1}	5.60745×10^{-2}	1.23029×10^{-1}	1.96250×10^{-1}	2.71725×10^{-1}
ACH_n	9.06873×10^{-2}	6.20802×10^{-2}	1.05881×10^{-1}	7.03087×10^{-2}	5.58433×10^{-2}	7.52276×10^{-2}	8.10944×10^{-2}	5.29042×10^{-2}	4.12821×10^{-2}	4.20941×10^{-2}	9.63773×10^{-2}	7.05465×10^{-2}
	2.23066×10^{-2}	3.08726×10^{-2}	2.26682×10^{-2}	3.24520×10^{-2}	4.29986×10^{-2}	-2.88362×10^{-2}	5.93145×10^{-2}	3.86039×10^{-2}	3.40167×10^{-2}	4.84843×10^{-2}	9.77476×10^{-2}	6.33234×10^{-2}
$ACOH$	5.50099×10^{-2}	4.45902×10^{-2}	7.50170×10^{-2}	4.74863×10^{-2}	4.06033×10^{-2}	6.83111×10^{-2}	7.10013×10^{-2}	4.02855×10^{-2}	2.99898×10^{-2}	4.53537×10^{-3}	(?)	3.66359×10^{-2}
	1.41345×10^{-3}	-6.96568×10^{-3}	6.85449×10^{-3}	1.42102×10^{-2}	2.12082×10^{-2}	-4.26791×10^{-2}	2.88578×10^{-2}	3.76714×10^{-2}	1.23743×10^{-2}	2.88017×10^{-2}	(?)	6.14349×10^{-2}

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Table 8. Bulk water activity measurements of the system water (1) + oxalic acid (2) + $(NH4)_2SO_4$ (3) at $T = 293.15$ K. Aqueous solution compositions are given in mass fractions (mf_j).

mf_2	mf_3	$a_w^{(x)}$
0.042792	0.006276	0.989
0.021864	0.006413	0.992
0.004451	0.006528	0.997
0.021317	0.031265	0.986
0.004337	0.031807	0.989
0.020671	0.060634	0.979
0.004204	0.061653	0.982

The accuracy of the water activity measurements is specified as $\pm 0.003 a_w$.

Table 9. Bulk water activity measurements of the system water (1) + malonic acid (2) + $(NH4)_2SO_4$ (3) at $T = 293.15$ K. Aqueous solution compositions are given in mass fractions (mf_j).

mf_2	mf_3	$a_w^{(x)}$
0.506526	0.006429	0.823
0.339160	0.008609	0.909
0.204210	0.010368	0.953
0.093090	0.011815	0.973
0.493827	0.031339	0.818
0.327869	0.041614	0.902
0.196078	0.049774	0.941
0.088889	0.056410	0.965
0.478821	0.060773	0.809
0.314770	0.079903	0.891
0.186782	0.094828	0.929
0.084142	0.106796	0.948
0.451389	0.114583	0.786
0.291480	0.147982	0.858
0.170604	0.173228	0.897
0.076023	0.192982	0.915

The accuracy of the water activity measurements is specified as $\pm 0.003 a_w$.

Table 10. Bulk water activity measurements of the system water (1) + glutaric acid (2) + (NH4)$_2$SO$_4$ (3) at $T = 293.15$ K. Aqueous solution compositions are given in mass fractions (mf_j).

mf_2	mf_3	$a_w^{(x)}$
0.394454	0.007889	0.941
0.245682	0.009827	0.965
0.115264	0.011526	0.980
0.236390	0.047278	0.951
0.110184	0.055092	0.967
0.225718	0.090287	0.932
0.104430	0.104430	0.967
0.207026	0.165621	0.898
0.094556	0.189112	0.918

The accuracy of the water activity measurements is specified as ±0.003a_w.

Table 11. Bulk water activity measurements of the system water (1) + succinic acid (2) + (NH4)$_2$SO$_4$ (3) at $T = 293.15$ K. Aqueous solution compositions are given in mass fractions (mf_j).

mf_2	mf_3	$a_w^{(x)}$
0.055368	0.006194	0.995
0.028472	0.006370	0.997
0.005827	0.006519	0.998
0.054029	0.030220	0.988
0.027765	0.031059	0.990
0.005679	0.031764	0.993
0.052444	0.058667	0.979
0.026928	0.060246	0.983
0.005504	0.061573	0.985

The accuracy of the water activity measurements is specified as $\pm 0.003 a_w$.

Table 12. Bulk water activity measurements of the system water (1) + adipic acid (2) + (NH4)$_2$SO$_4$ (3) at $T = 293.15$ K. Aqueous solution compositions are given in mass fractions (mf_j).

mf_2	mf_3	$a_w^{(x)}$
0.005827	0.006519	0.992
0.005679	0.031764	0.985
0.005504	0.061573	0.979

The accuracy of the water activity measurements is specified as $\pm 0.003 a_w$.

Table 13. Bulk water activity measurements of the system water (1) + maleic acid (2) + Ca(NO$_3$)$_2$ (3) at T = 293.15 K. Aqueous solution compositions are given in mass fractions (mf_j).

mf_2	mf_3	$a_{\mathrm{w}}^{(x)}$
0.307692	0.053450	0.903
0.181818	0.063168	0.942
0.100000	0.069485	0.955
0.052632	0.073142	0.970
0.166667	0.115808	0.916
0.090909	0.126336	0.938
0.047619	0.132352	0.948
0.142857	0.198528	0.865
0.076923	0.213799	0.891
0.040000	0.222351	0.900
0.111111	0.308821	0.784
0.058824	0.326987	0.801
0.030303	0.336895	0.813

The accuracy of the water activity measurements is specified as ±0.003a_{w}.

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Table 14. Bulk water activity measurements of the system water (1) + maleic acid (2) + Mg(NO$_3$)$_2$ (3) at $T = 293.15$ K. Aqueous solution compositions are given in mass fractions (mf_j).

mf_2	mf_3	$a_\mathrm{w}^{(x)}$
0.307692	0.044495	0.926
0.181818	0.052585	0.943
0.100000	0.057843	0.979
0.052632	0.060888	0.994
0.047619	0.110178	0.947
0.040000	0.185099	0.886
0.030303	0.280452	0.777

The accuracy of the water activity measurements is specified as ±0.003a_w.

Table 15. Bulk water activity measurements of the system water (1) + maleic acid (2) + NH$_4$Br (3) at $T = 293.15$ K. Aqueous solution compositions are given in mass fractions (mf_j).

mf_2	mf_3	$a_w^{(x)}$
0.320000	0.040000	0.950
0.190476	0.047619	0.976
0.105263	0.052632	0.987
0.055556	0.055556	1.000
0.052632	0.105263	0.969
0.047619	0.190476	0.930
0.040000	0.320000	0.890

The accuracy of the water activity measurements is specified as ±0.003a_w.

Table 16. Bulk water activity measurements of the system water (1) + malonic acid (2) + NH$_4$NO$_3$ (3) at T = 293.15 and 303.15 K. Aqueous solution compositions are given in mass fractions (mf_j).

mf_2	mf_3	$a_w^{(x)}$ (293.15 K)	$a_w^{(x)}$ (303.15 K)
0.493827	0.012346	0.835	0.826
0.327869	0.016393	0.920	0.912
0.196078	0.019608	0.985	0.948
0.108696	0.021739	0.978	0.964
0.470588	0.058824	0.807	0.800
0.307692	0.076923	0.890	0.868
0.181818	0.090909	0.932	0.920
0.100000	0.100000	0.948	0.938
0.444444	0.111111	0.771	0.759
0.285714	0.142857	0.859	0.852
0.166667	0.166667	0.897	0.888
0.090909	0.181818	0.912	0.907
0.400000	0.200000	0.725	0.711
0.250000	0.250000	0.801	0.776
0.142857	0.285714	0.833	0.821
0.076923	0.307692	0.857	0.826

The accuracy of the water activity measurements is specified as ±0.003a_w.

Table 17. Bulk water activity measurements of the system water (1) + malonic acid (2) + Na$_2$SO$_4$ (3) at $T = 293.15$ and 303.15 K. Aqueous solution compositions are given in mass fractions (mf_j).

mf_2	mf_3	$a_w^{(x)}$ (293.15 K)	$a_w^{(x)}$ (303.15 K)
0.493827	0.012346	0.799	0.772
0.327869	0.016393	0.908	0.857
0.196078	0.019608	0.952	0.927
0.108696	0.021739	0.989	0.948
0.470588	0.058824	0.782	0.789
0.307692	0.076923	0.879	0.890
0.181818	0.090909	0.952	0.901
0.100000	0.100000	0.973	0.920

The accuracy of the water activity measurements is specified as ±0.003a_w.

Table 18. Bulk water activity measurements of the system water (1) + malonic acid (2) + NaCl (3) at $T = 293.15$ and $303.15\,\text{K}$. Aqueous solution compositions are given in mass fractions (mf_j).

mf_2	mf_3	$a_\text{w}^{(x)}$ (293.15 K)	$a_\text{w}^{(x)}$ (303.15 K)
0.493827	0.012346	0.807	0.817
0.327869	0.016393	0.905	0.910
0.196078	0.019608	0.949	0.951
0.108696	0.021739	0.970	0.966
0.470588	0.058824	0.770	0.775
0.307692	0.076923	0.841	0.853
0.181818	0.090909	0.882	0.893
0.100000	0.100000	0.910	0.913

The accuracy of the water activity measurements is specified as $\pm 0.003 a_\text{w}$.

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Table 19. Bulk water activity measurements of the system water (1) + malonic acid (2) + LiNO$_3$ (3) at $T = 293.15$ and 303.15 K. Aqueous solution compositions are given in mass fractions (mf_j).

mf_2	mf_3	$a_w^{(x)}$ (293.15 K)	$a_w^{(x)}$ (303.15 K)
0.493827	0.012346	0.806	0.805
0.327869	0.016393	0.893	0.911
0.196078	0.019608	0.943	0.944
0.108696	0.021739	0.964	0.967
0.470588	0.058824	0.742	0.761
0.307692	0.076923	0.830	0.843
0.181818	0.090909	0.884	0.894
0.100000	0.100000	0.907	0.915
0.444444	0.111111	0.666	0.691
0.285714	0.142857	0.745	0.759
0.166667	0.166667	0.798	0.809
0.090909	0.181818	0.811	0.826

The accuracy of the water activity measurements is specified as $\pm 0.003 a_w$.

Table 20. Bulk water activity measurements of the system water (1) + malonic acid (2) + NH$_4$Br (3) at $T = 293.15$ and 303.15 K. Aqueous solution compositions are given in mass fractions (mf_j).

mf_2	mf_3	$a_w^{(x)}$ (293.15 K)	$a_w^{(x)}$ (303.15 K)
0.493827	0.012346	0.821	0.823
0.327869	0.016393	0.913	0.915
0.196078	0.019608	0.952	0.947
0.108696	0.021739	0.978	0.972
0.470588	0.058824	0.788	0.776
0.307692	0.076923	0.880	0.871
0.181818	0.090909	0.918	0.913
0.100000	0.100000	0.946	0.937
0.090909	0.181818	0.900	0.898

The accuracy of the water activity measurements is specified as ±0.003a_w.

Table 21. Measured solubility limits of 2,4-dihydroxybenzaldehyde in different ternary solutions of water (1) + 2,4-dihydroxybenzaldehyde (2) + salt (3) at $T = 298.15$ K. Aqueous solution compositions are given in mass fractions (mf_j).

mf_2	mf_3	mf_2	mf_3
salt-free			
0.004975	0.000000		
Ca(NO$_3$)$_2$ (3)		Mg(NO$_3$)$_2$ (3)	
0.008090	0.076581	0.006842	0.063851
0.006261	0.138099	0.006126	0.115015
0.003024	0.230915	0.004860	0.191936
0.002991	0.296901	0.003862	0.247022
NH$_4$Br (3)		Na$_2$SO$_4$ (3)	
0.007021	0.058411	0.004879	0.024271
0.005173	0.110536	0.004917	0.058534
0.005003	0.198999	0.003940	0.110673
NaCl (3)			
0.005248	0.024262		
0.004567	0.058555		
0.004623	0.110597		
0.003607	0.199279		

The estimated error of the stated SLE compositions is < 20 % (by weight).
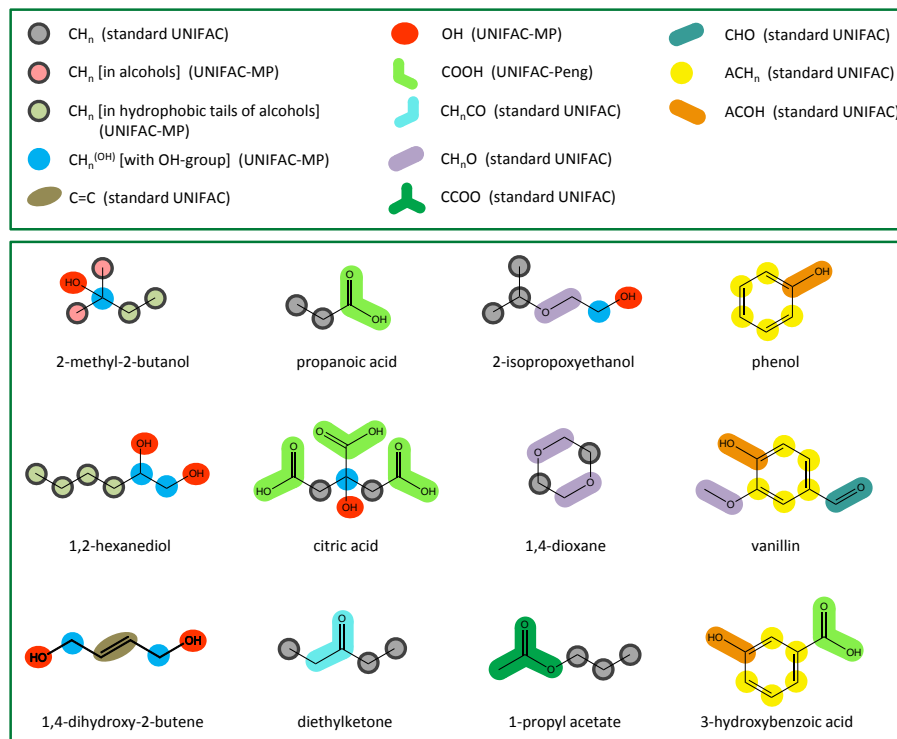
Fig. 1. Upper box: complete list of types of organic functional main groups used in AIOMFAC. AIOMFAC follows the UNIFAC naming convention for functional groups (see also Fig. 8). Besides the functional groups and associated interaction parameters of standard UNIFAC (Hansen et al., 1991), specific groups of Marcolli and Peter (2005) (UNIFAC-MP) and of Peng et al. (2001) (UNIFAC-Peng) are used as indicated. AIOMFAC middle-range main group ↔ ion interactions involving the specific alkyl groups CH_n [in hydrophobic tails of alcohols] and CH_n [in alcohols] are described with the same parameters as CH_n (standard UNIFAC) ↔ ion interactions, denoted by the common outline color. Lower box: examples.

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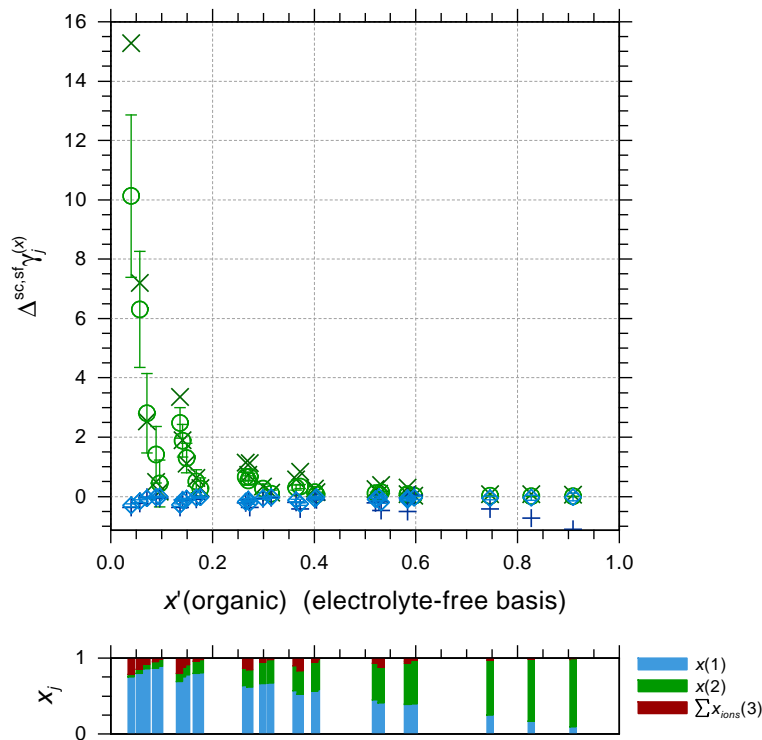
Fig. 2. Activity coefficient deviations $\Delta^{sc,sf}\gamma_j^{(x)}$ of salt-free vs. salt-containing mixtures in the water (1) + 2-propanol (2) + LiCl (3) system derived from isobaric VLE data at 354–358 K. Experimental data ($\times$, $+$) by Lin et al. (1993) and calculated values ($\bigcirc$, $\diamond$) are shown in blue for water and in green for 2-propanol. The error bars represent the model sensitivity to a composition variation by $x^{tol} = 0.01$. The mixture compositions with respect to completely dissociated LiCl are shown in the bar graphs.
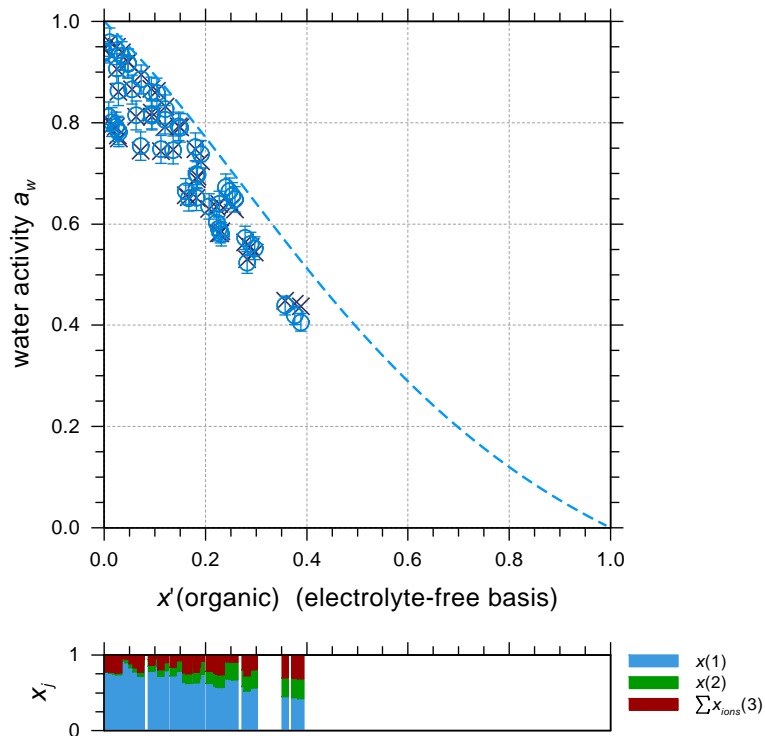
Fig. 3. Water activities in the ternary system water (1) + malonic acid (2) + $(NH_4)_2SO_4$ (3) at 298 K. Experimental bulk a_w data ($\times$) by Salcedo (2006) and corresponding calculated values ($\bigcirc$) at various mixture compositions, as shown in the bar graphs. The error bars represent the model a_w-sensitivity to a composition variation by $x^{tol} = 0.01$. The dashed curve shows the calculated water activity of the salt-free solvent mixture.
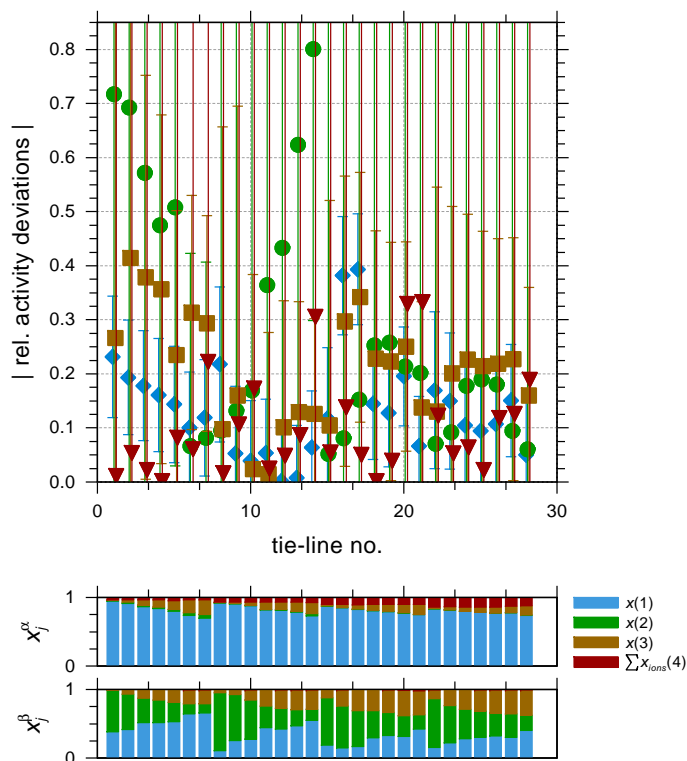
Fig. 4. Calculated relative activity deviations in the quaternary LLE system water (1) + 4-methyl-2-pentanone (2) + acetic acid (3) + NaCl (4) at 308 K. Compositions of the two phases α and β are given in the bar graphs at each tie-line, measured by Govindarajan and Sabarathinam (1995). Relative activity deviations and corresponding model sensitivities (error bars) are shown for water (◆), 4-methyl-2-pentanone (●), acetic acid (■), and rel. IAP deviations for NaCl (▼). For clarity, symbols of the different components at a tie-line are shifted slightly in x-axis direction.
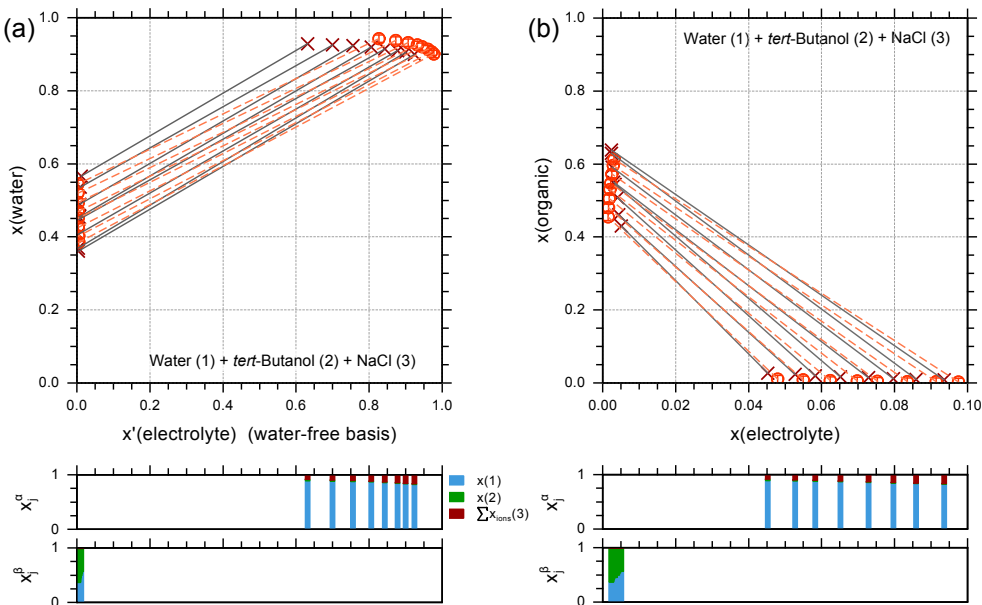
Fig. 5. Experimental and computed LLE phase compositions of the ternary system water (1) + *tert*-butanol (2) + NaCl (3) at 298 K. Measured tie-line data ($\times$) by Gomis et al. (1996) and computed compositions ($\bigcirc$) using AIOMFAC with the phase separation prediction module (Zuend et al., 2010). **(a)** Phase diagram where the abscissa represents the water-free "dry" molar mixture composition, x'(NaCl). The solid gray and dashed red lines indicate coexisting phase compositions of the measured and calculated compositions, respectively (non-standard tie-lines in this coordinate system). **(b)** Phase diagram of the same system, plotted on mole fraction axis, x(NaCl) vs. x(*tert*-butanol). In this coordinate system, tie-lines maintain their standard meaning, i.e., initial (unstable) and stable end points are collinear. In **(b)**, experimental and calculated tie-lines intersect at the initial compositions, x_j^{init}, used for the phase separation computations.

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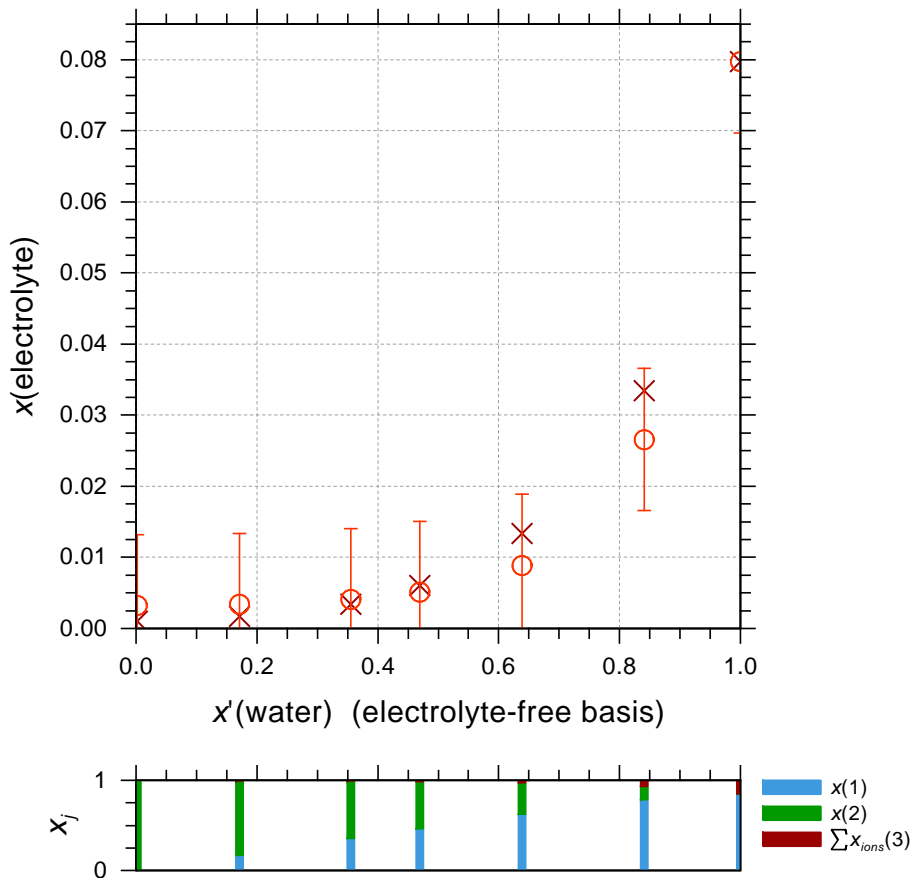
Fig. 6. Experimental and calculated SLE compositions of the system water (1) + 2-ethoxyethanol (2) + KCl (3) at 298 K, saturated with KCl. SLE composition measurements (✕) by (Chiavone-Filho and Rasmussen, 1993) and calculated solubility limits (○) using the IAP$_{KCl}$ of the saturated binary water + KCl solution as reference. Error bars represent $x^{tol} = 0.01$.
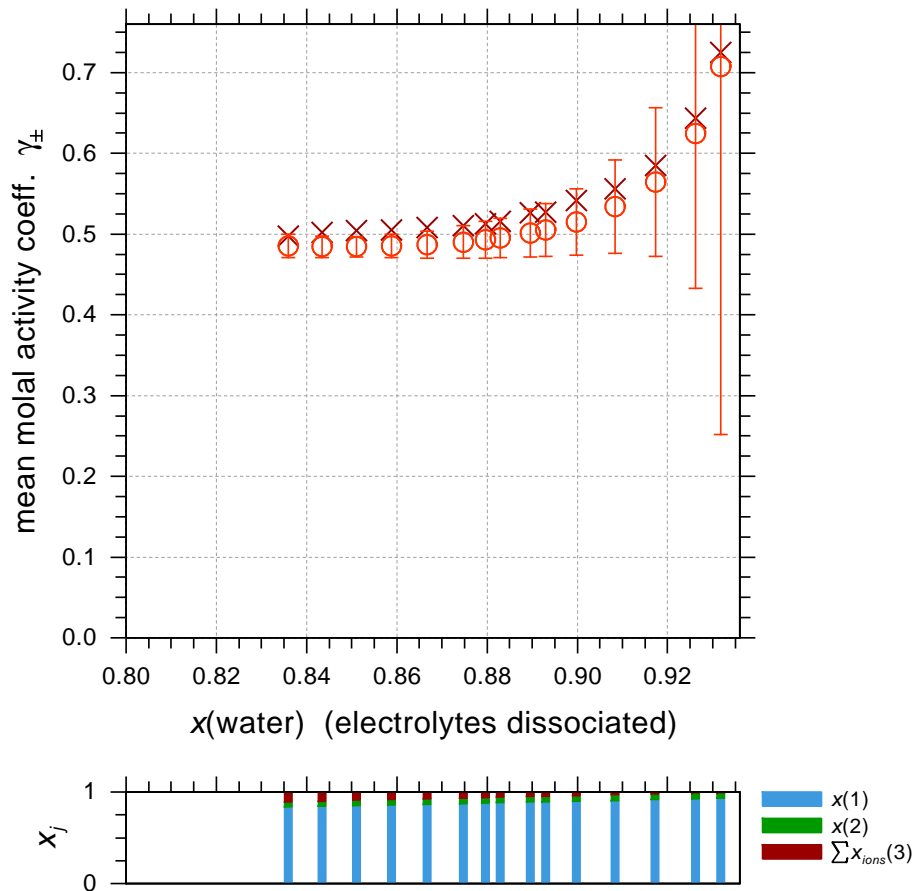
Fig. 7. Mean molal activity coefficients $\gamma_\pm$ of KCl in the system water (1) + ethanol (2) + KCl (3) at 298 K. Experimental values (✕) derived from EMF measurements by Lopes et al. (1999), calculated $\gamma_\pm$ values (○) and corresponding activity coefficient sensitivities (error bars) are with regard to the mixed solvent reference state definition.

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group name	ions → main groups ↓	H^+	Li^+	Na^+	K^+	NH_4^+	Mg^{2+}	Ca^{2+}	Cl^-	Br^-	NO_3^-	HSO_4^-	SO_4^{2-}
alkyl	CH_n	19	31	184	68	90	16	35	256	35	43	5	104
alkyl bonded to hydroxyl group	$CH_n^{(OH)}$	10	19	91	40	43	13	20	140	21	23	1	51
hydroxyl	OH	10	19	91	40	43	13	20	140	21	23	1	51
carboxyl	COOH	4	9	47	33	48	6	6	66	9	18	4	56
ketone	CH_nCO	4	2	40	9	3	2	2	37	4	7		14
aldehyde	CHO		1	4	1	1		1	4	1	1		2
ether	CH_nO	2	7	24	14	4	1	5	45	5	2	1	4
ester	CCOO		4	14	2			5	19	4	1		1
alkenyl	C=C	1	1	4	1	7	1	1	6	1	4	1	4
aromatic hydrocarbon	ACH_n	7	8	19	26	4	5	2	40	8	6	1	16
aromatic carbon-alcohol	ACOH	3	7	14	24	1	5	1	32	6	4		13

Fig. 8. Distribution of datasets for the determination of organic main group ↔ ion interaction parameters. The number of different datasets associated with each interaction pair is shown. Percentile-wise coloring based on the number of datasets suggests the degree of confidence (based only on statistical considerations) in the determined interaction parameters: blue (low confidence) to red (high confidence).

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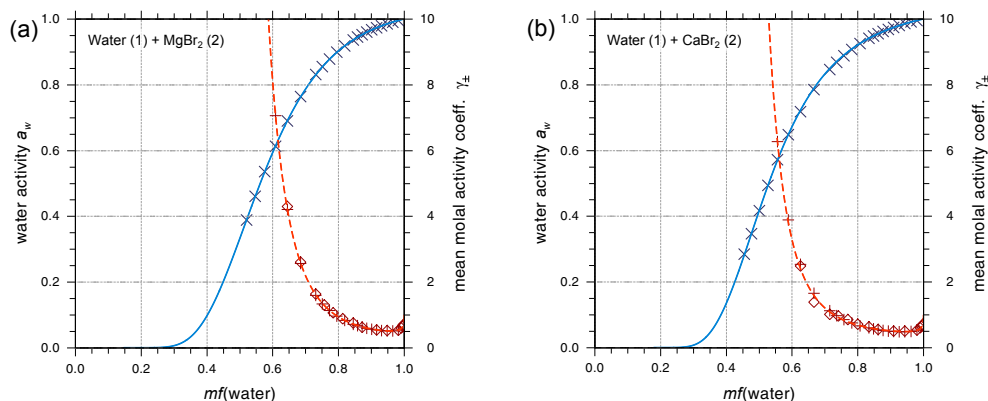Tables | Figures

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Fig. 9. Water activities and mean molal activity coefficients of the binary aqueous **(a)** MgBr$_2$ and **(b)** CaBr$_2$ systems at 298 K. The curves show calculated water activities in blue and mean molal activity coefficients of the electrolytes in red (right y-axis), resulting from the AIOMFAC parameter fit to measurements (symbols), vs. mass fraction (mf) of water. Experimental data in (a) and (b): a_w ($\times$) and $\gamma_\pm$ ($+$) by Robinson and Stokes (2002), and $\gamma_\pm$ ($\diamond$) by Zaytsev and Aseyev (1992).

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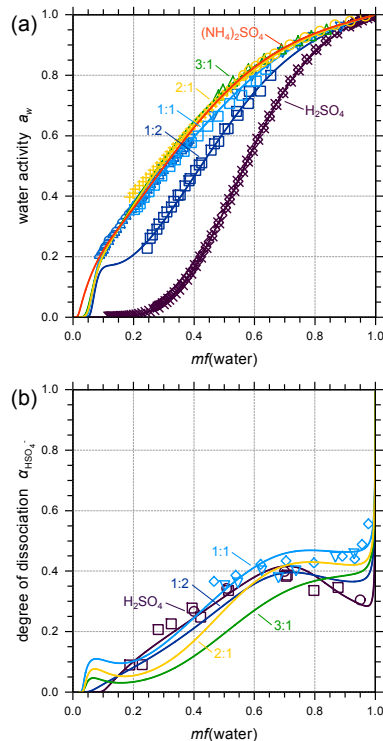
Fig. 10. Calculated and experimental water activities and degree of dissociation of the bisulfate ion in aqueous solutions of sulfuric acid and mixtures of ammonium sulfate and sulfuric acid (i.e., the degree to which the second ionization stage, $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$, of sulfuric acid is established, see Zuend et al., 2008). The molar ratio of $(NH_4)_2SO_4 : H_2SO_4$ is indicated for the different mixtures. **(a)** Calculated water activities (curves) and measured bulk and EDB water activity data (symbols) at room temperature; Robinson and Stokes (2002) ($\times$), Staples (1981) ($\diamond$), Kim et al. (1994) ($\square$), Tang and Munkelwitz (1977) ($\triangledown$), Spann (1984) ($\frown$), Tang and Munkelwitz (1994) ($\triangle$), Zuend et al. (2008) ($\bigcirc$), Zardini et al. (2008) ($+$). Calculated a_w of $(NH_4)_2SO_4$ is shown for comparison. **(b)** Corresponding degrees of dissociation of the bisulfate ion, $\alpha_{HSO_4^-}$ (Zuend et al., 2008), as a function of the mass fraction of water. Measured $\alpha_{HSO_4^-}$ of aqueous sulfuric acid by Knopf et al. (2003) ($\bigcirc$) and Myhre et al. (2003) ($\square$), and of the 1 : 1 mixture by Young et al. (1959) ($\diamond$) and Dawson et al. (1986) ($\triangledown$).
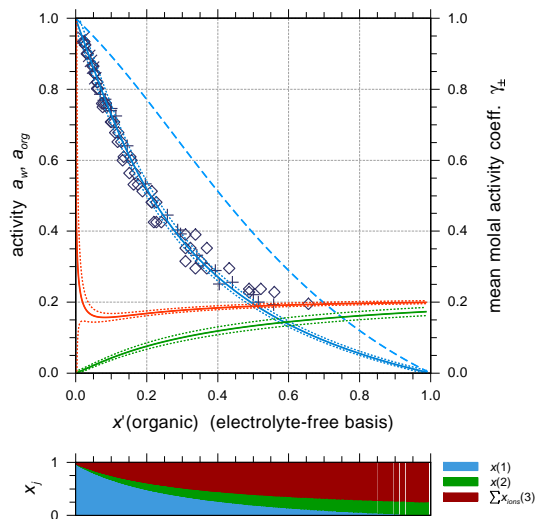
Fig. 11. Water activity measurements and AIOMFAC calculations for the system water (1) + malonic acid (2) + $(NH_4)_2SO_4$ (3). All mixtures are at a 1 : 1 molar ratio of malonic acid : $(NH_4)_2SO_4$. Experimental bulk data for a_w at 295 K (+) by Choi and Chan (2002), EDB data at 298 K (+) by Ling and Chan (2008), and micro-Raman data at 297 K (◇) by Yeung and Chan (2010). Calculated curves at 298 K: a_w (solid blue), a_{org} of malonic acid (solid green), $\gamma_\pm$ of $(NH_4)_2SO_4$ (solid red), and a_w of salt-free mixture (dashed blue). The dotted curves bordering the solid curves in the corresponding colors represent AIOMFAC sensitivities with respect to $x^{tol} = 0.01$.
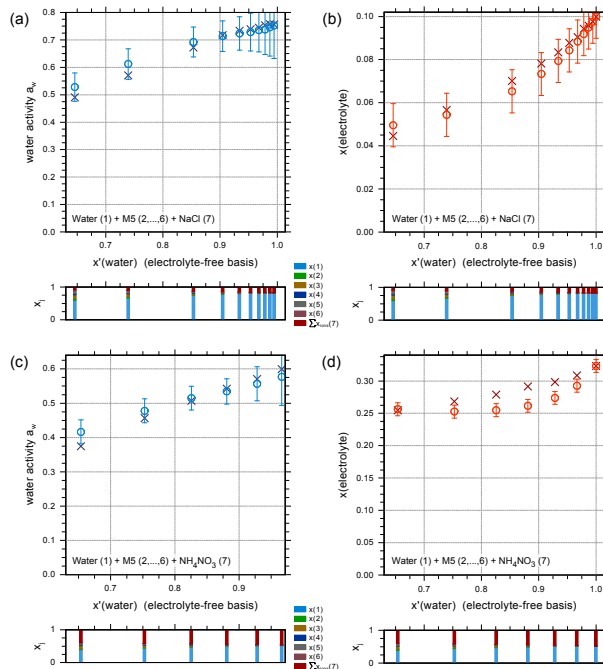
Fig. 12. Water activities and salt solubilities in saturated multicomponent solutions of water (1) + M5 (2,…,6) + NaCl (7) and water (1) + M5 (2,…,6) + NH$_4$NO$_3$ (7) at 298 K, where M5 = malic acid (2) + malonic acid (3) + maleic acid (4) + glutaric acid (5) + methylsuccinic acid (6). Panels **(a)** and **(c)** show measured bulk a_w data ($\times$), calculated values ($\bigcirc$), and activity sensitivities (error bars) for the two systems. Panels **(b)** and **(d)** show corresponding measured ($\times$) and calculated ($\bigcirc$) salt solubility limits in terms of mole fractions of the salt on the basis of undissociated electrolyte. Experimental data by Marcolli et al. (2004a). Note the different axis scalings.

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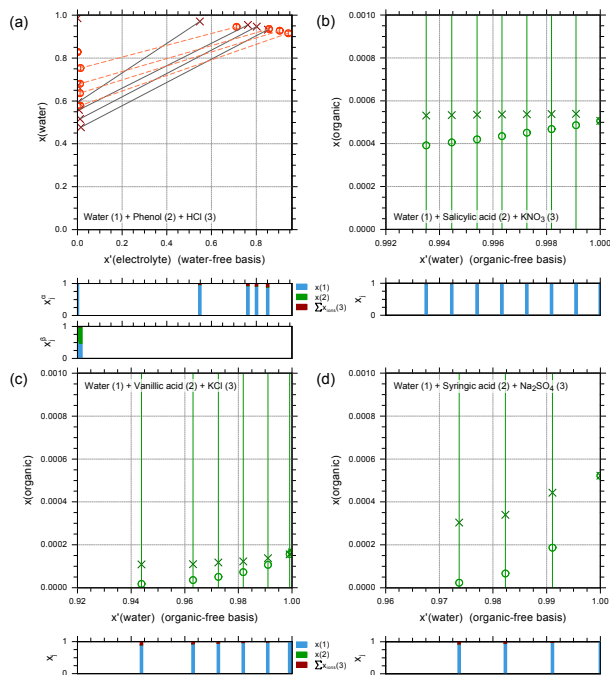
Fig. 13. Ternary systems containing multifunctional phenolic compounds. Experimental values are given by symbols (×) and respective AIOMFAC calculations by (○). **(a)** LLE of water (1) + phenol (2) + HCl (3) at 285 K. LLE composition measurements by Schreinemakers and van den Bos (1912). **(b)** Solubility limits of salicylic acid in aqueous KNO_3 solutions at 308 K. Measurements by Sugunan and Thomas (1995). **(c)** Solubility limits of vanillic acid in aqueous KCl solutions at 298 K. Measurements by Noubigh et al. (2007b). **(d)** Solubility limits of syringic acid in aqueous Na_2SO_4 solutions at 298 K. Measurements by Noubigh et al. (2008).
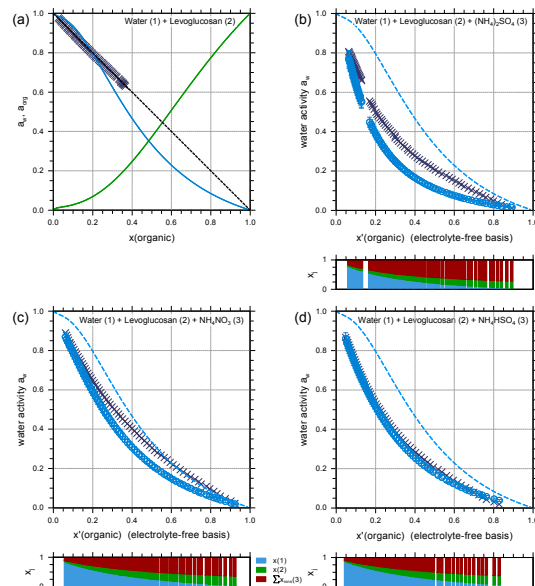
Fig. 14. Water activities of the binary and ternary water (1) + levoglucosan (2) + electrolyte (3) systems at 291 K. **(a)** In case of the binary system, the EDB water activity data (×) closely matches an ideal solution (dashed line). The AIOMFAC (UNIFAC) a_w-curve (blue line) shows larger deviations. The green curve shows the corresponding calculated activity of levoglucosan. **(b)**, **(c)**, and **(d)** Ternary systems containing the electrolytes ammonium sulfate, ammonium nitrate, and ammonium bisulfate, respectively, mixed at a molar ratio of 1 : 1 with levoglucosan. Symbols show the experimental water activity data (×) and corresponding AIOMFAC calculations (○). Error bars of the experimental data are smaller than the symbol size. The dashed, blue curve shows the electrolyte-free a_w model curve for comparison. Measurements by Lienhard et al. (2011).

Extended parameterization of the AIOMFAC model

A. Zuend et al.

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